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The Toxicity of Bromochloromethane (Methylene Chlorobromide) as Determined on Laboratory Animals

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Introduction

ALTHOUGH bromochloromethane, CH_2BrCl, is an old compound, interest in its toxicity results primarily from its recent use as a vaporizing liquid fire extinguisher. It was developed for the German Air-Force during World War II by I. G. Farbenindustrie A.G. It is considerably less toxic than methyl bromide and more effective than carbon tetrachloride, both of which were used in fire extinguishers on military aircraft. It has been referred to as CB and methylene chlorobromide but these two designations have fallen into disuse and bromochloromethane and BCM are now generally used. When the information about bromochloromethane was disclosed after the German surrender, considerable interest was expressed in its use as a replacement for carbon tetrachloride in home and industrial fire extinguishers as well as in aircraft. It is of interest, then, to compare the toxicity of bromochloromethane with that of carbon tetrachloride, particularly on the basis of acute vapor exposures since this is the type of exposure humans are likely to receive when extinguishing fires.

The only reference to the toxicity of bromochloromethane to humans which was found in the literature is by Hirokawa.[1] In this incident, three individuals were exposed to a mixture of methylene chloride and methylene bromide as well as bromochloromethane while manufacturing bromochloromethane. Exposures were very severe as no precautions were taken to prevent injury. Because of the mixture of materials involved, it is impossible to interpret the significance of this data, and the report is of doubtful value.

Although there are considerable published data about the toxicity of bromochloromethane to animals, the data are somewhat inconsistent due to the very limited nature of some of the studies that have been reported. The most complete study was reported jointly by Svirbely *et al.*[2] and Highman *et al.*[3] Their reports include the results of single and repeated exposure as well as the results of oral administrations to mice. These workers found the acute oral LD_{50} for mice to be 4.3 g/kg. They found the material to be more toxic to mice from acute inhalation than carbon tetrachloride and observed a large number of delayed deaths. They concluded that the material was "a narcotic agent of moderate intensity but of prolonged duration." They also reported that the material caused only slight changes in the liver as contrasted to cirrhosis resulting from exposure to carbon tetrachloride. Svirbely and Highman found that rats showed fewer pathological changes than mice and that guinea pigs were intermediate in response.

In order to determine the chronic toxicity of bromochloromethane, Svirbely, Highman and coworkers[2, 3] exposed a group of animals consisting of 20 male rats, three female rabbits and two female dogs to a concentration of 1000 ppm, seven hours per day for a total of 67 exposures in 14 weeks. No significant changes were seen except for a slight increase in the amount of hemosiderin in the spleen and kidneys of the dogs and in the spleen of the rats, and an increase in the amount of fat in the kidneys of dogs. No evidence of cirrhosis of the liver was seen. Inorganic blood bromide levels were elevated in the dogs. After 13 weeks of exposure, bromide ion levels in the blood were of the order of 300 to 360 mg per 100 ml of blood and were not assumed to have reached a maximum.

Underwriters' Laboratories[4] have reported rather limited toxicological data on bromochloromethane as compared to carbon tetrachloride. Using guinea pigs as their test animals, they concluded that the two materials were essentially equal in acute vapor toxicity and in the toxicity of their thermal decomposition products. Unfortunately, this study was designed for testing refrigerants, not fire extinguishers. Only small groups of animals (2 to 3 guinea pigs) were used for each exposure and only very limited pathological examinations of the animals were made.

The Army Chemical Center[5] in a comparative

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study of several vaporizing liquid extinguishers reported that rats survived one 15-minute exposure to 54,000 ppm of bromochloromethane, whereas, 65,175 ppm was lethal. In another report by the Army Chemical Center, Comstock, Fogelman and Oberst[6] found that no deaths occurred during a 15-minute exposure of rats to 27,000 ppm or less. However, delayed deaths occurred after 15-minute exposures to 22,000 ppm and higher. The delayed deaths were attributed to pulmonary injury. No pathological findings due to exposure were seen in rats sacrificed 14 days after exposure to 27,000 ppm or less. Rats, which survived exposure to concentrations above 27,000 ppm showed diffuse tracheitis and interstitial pneumonitis but no liver or kidney pathology was seen 14 days after exposure.

Comstock and Oberst[7] also reported the results of a comparative study of four fire extinguishing fluids in which 20 mice and 40 rats were exposed for 15 minutes to a concentration of 76 mg/liter (14,000 ppm). No deaths were observed in the mice during a 14 day observation period but two rats died during this same period of time. Since the deaths apparently occurred 13 days after exposure it is difficult to attach significance to so low a mortality.

The experiments reported herein were started before any of the previously discussed data were published and have yielded results which may help to clarify some of the confusion in the published data. In this study, considerable emphasis has been placed on acute exposures particularly as related to the quantitative aspects of nonlethal injury. In addition, results of repeated exposure of animals to 1000, 500, 370 and 130 ppm for two to six months are also reported as well as results of oral intubation to rats, topical application to the skin and eyes of rabbits, and acute skin absorption studies on rabbits. The hazards of single and repeated exposures are evaluated and handling precautions are discussed. Blood bromide concentrations are reported for many of the exposures and an attempt is made to reconcile apparent discrepancies between the values reported by commonly used methods for determining blood bromide.

Experimental Procedures

Materials Tested

Bromochloromethane, CH_2BrCl, is a colorless liquid with a density of 1.92 g/ml at 25°C, a freezing point of −88.08°C and a boiling point of 68.11°C at 760 mm Hg. The vapor pressure at 25°C is 147.17 mm Hg and a saturated atmosphere at 25°C consists of about 19% bromochloromethane by volume.

The samples used in these studies were obtained from production lots and all but one were shown by infrared analysis to be over 99% CH_2BrCl, the balance being methylene chloride, CH_2Cl_2 and methylene bromide, CH_2Br_2. The other sample contained 98% CH_2BrCl, 0.6% CH_2Cl_2, 0.4% CH_2Br_2 and 1.0% of a corrosion inhibitor.

Source and Feeding of Animals and Equipment Used

The housing, diet and care of animals as well as the exposure equipment and techniques used in this study have been adequately described in previous publications from this laboratory.[8] Single vapor exposures were conducted in 160-liter capacity glass-walled chambers and the repeated exposures in 1700-liter capacity water-sealed chambers. The size of the exposure groups is shown in the tables. All groups of animals, including the controls, were carefully matched as to age, weight, sex and condition.

This study was conducted in five phases, the first phase being designed to determine the minimum single exposure intensities resulting in essentially complete mortality and the maximum single exposure intensities resulting in essentially no mortality. This study was done using male and female rats. The second phase was to determine the maximum single exposure intensities which resulted in no detectable organic injury. This study was conducted on female rats. The third phase consisted of repeated 7-hour daily exposures of several species of animals to 1000 and 500 ppm. The fourth phase consisted of repeated 7-hour exposures of female rats and one male and one female dog to 370 ppm, and the fifth phase, repeated 7-hour exposure of female rabbits to 130 ppm.

Single Vapor Exposures, Phase 1 and 2

In order to determine the conditions causing essentially 100% and 0% mortality, the following procedure was used. Groups of male and female rats were weighed before exposure. The exposures were made by introducing the groups of rats into established vapor concentrations by quickly dropping them through entry tubes on the top of the 160-liter chambers. Concentrations were checked from time to time before and during exposure by combustion analysis. The results were generally within 10% of the calculated values. The animals were observed during exposure and until death occurred or until consciousness was regained. The rats were generally weighed the day following exposure and at intervals for two weeks thereafter or until it was

apparent that all animals had recovered and were gaining weight normally.

In the second phase of the experiment, female rats were used to determine the maximum single exposures resulting in no detectable organic injury. These animals were carefully matched on the basis of weight and condition. They were exposed in the same manner as those in phase one. After exposure they were returned to their cages where food and water were available. The food was subsequently withdrawn late that afternoon so that the rats were in a fasted condition when sacrificed the following day. At autopsy the exposed rats, as well as the control groups, were killed by decapitation and gross pathological examination made. After gross observation, the lungs, heart, liver, kidneys and spleen were removed and weighed. Portions of these organs, as well as the pancreas and adrenals were fixed in formalin and stained with hematoxylin-eosin for microscopic examination. In addition to the hematoxylin-eosin stain, a special fat stain, Oil Red O, was used on many of the sections. Since the exposures in this phase were made in three series, each series has its own set of controls: A, B or C. The control group for each experimental group is indicated in Table II which summarizes the results of these exposures.

Repeated Vapor Exposures, Phase 3, 4 and 5

Three matched groups of animals consisting of 20 male and 20 female rats, 10 male and 10 female guinea pigs, two male and two female rabbits, and 10 female mice were selected. The first group was exposed 79 to 82 times in 114 days to 500 ppm bromochloromethane in air (average 490 ppm by analysis). The second group was similarly exposed to an average concentration of 1000 ppm (average 1010 ppm by analysis). The exposures were for seven hours per day and generally given five days a week. The third group was maintained in the animal quarters at all times as unexposed controls. The animals were weighed twice a week until it was evident that growth was essentially normal and once a week thereafter. Growth curves and mortality records were kept for all the animals. Terminal hematological examinations were made on representative animals, Table V. Determinations of blood bromide, blood urea-nitrogen (BUN) and blood non-protein-nitrogen (NPN) were made as indicated in Table IV. At autopsy, all animals were killed the day following their last exposure. The rats were fasted overnight, then they and all the other animals were killed by decapitation. Blood from representative animals was collected for subsequent chemical analysis. After gross pathological examination was made, the lungs, heart, liver, kidney, spleen and testes were removed and weighed. The final organ weights are given in Table III. Portions of these organs, as well as the pancreas and adrenals were examined microscopically. Where applicable, the "t" test[9] was used to determine the significance of organ weight differences. A probability (P) of 0.05 or less was considered as significant.

Since it was evident that female rats were the only group which was significantly affected by exposures to 500 ppm, it was deemed desirable to expose another group of female rats to 400 ppm (370 ppm by analysis) and to observe their response. One dog of each sex was included in this experiment since this species had not been exposed to the higher concentrations. The same general procedures were followed during this experiment as were used during the exposures to 500 and 1000 ppm, except that two sets of controls were maintained. One set (unexposed controls) was kept in the animal quarters and the other control group (air-exposed controls) received exposures to room air in a chamber similar to that used for the chemical exposure. Preexposure and terminal hematological values for the dog are given in Table VI. Blood bromide levels are given in Table IV and final organ weights are summarized in Table III.

In order to follow the bromide level in the blood an additional small experiment, phase 5, was conducted in which four female rabbits received repeated 7-hour daily exposures to 130 ppm of bromochloromethane. A total of 45 exposures was given in a 63 day period. Two to three ml of blood was taken by cardiac puncture as indicated in Table VII. Routinely the samples were transferred from the syringe to an oxalated vial and the whole blood analyzed by the ashing method described by Shrader.[10] However, sufficient blood was drawn so that one set of samples could be analyzed by a gold chloride method as well.[11]

Because of apparent inconsistencies in the blood bromide levels reported by the different analytical methods, an attempt was made to design a simple study to compare the gold chloride method of Wuth[11] with the ashing technique of Shrader.[10] Eight healthy rabbits were given various dosages of a 50% solution of sodium bromide in water by means of a stomach tube. The doses given were 2.0, 1.0, 0.5 and 0.0 g of the salt per kg of body weight. Twenty-one hours later 20–50 ml of blood was removed by cardiac puncture. Two 3-ml samples of the blood were placed in oxalated bottles to be analyzed by the ashing

technique.[10] The balance of each sample was transferred to a centrifuge tube, allowed to stand for several minutes, and then centrifuged to obtain the serum. The serum from each animal was divided and analyzed by the gold chloride method[11] as well as by ashing.[10] One set of serum samples was analyzed by two medical laboratories using the gold chloride technique. The results are summarized in Table VIII. All values for blood bromide in this report are in terms of Br^-/100 ml unless specifically stated as otherwise.

Results

RESULTS OF ORAL ADMINISTRATION, TOPICAL APPLICATION TO THE SKIN AND EYES, AND SKIN ABSORPTION STUDIES

Aliquots of a 50% solution of bromochloromethane in corn oil were fed to groups of five male rats. All animals survived a dose of 5 g/kg and all animals died within 24 hours after a dose of 7 g/kg.

When the undiluted liquid was confined for 24 hours on the clipped belly using a modified Draize technique,[12] four out of four rabbits survived a dose of 5 g/kg with only a slight loss in body weight occurring. No higher dosages were administered. Confining the material on the skin such as was done in this type of exposure resulted in a burn and denaturation of the skin. If allowed to evaporate, the material had only the typical defatting effect of a solvent. The material had a moderate effect when instilled in the eyes of two rabbits. Considerable swelling of the conjunctiva and slight transitory irritation of the cornea occurred.

TABLE I

Mortality of Rats Exposed to Various Concentrations of Bromochloromethane for Single Periods of Time

Calc. vapor conc. ppm	Duration of exposure hours	Mortality Ratio		
		Males	Females	Both sexes
80,000	0.2	10/10	10/10	20/20
	0.1	0/10	0/10	0/20
40,000	0.6	10/10	10/10	20/20
	0.4	10/10	10/10	20/20
	0.3	6/10	8/10	14/20
	0.2	3/10	3/10	6/20
	0.1	0/15	0/15	0/30
20,000	2.0	10/10	10/10	20/20
	1.5	10/10	9/10	19/20
	1.0	9/10	6/10	15/20
	0.5	0/10	1/10	1/20
	0.4	2/10	0/10	2/20
	0.3	1/10	0/10	1/20
10,000	6.0	10/10	10/10	20/20
	4.0	6/10	5/10	11/20
	2.0	1/10	1/10	2/20
	1.5	1/10	0/10	1/20
	1.0	0/10	1/10	1/20
5,000	7.0	0/11	0/11	0/22

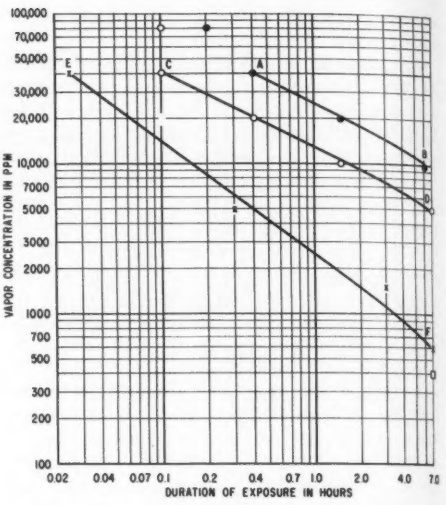

FIGURE 1. Vapor Toxicity of Bromochloromethane. The solid circles, Line AB, represent minimum exposures resulting in essentially total mortality. The open circles, Line CD, represent maximum exposures resulting in essentially no mortality. The X's represent the maximum exposures judged to be without detectable organic injury. The square at 400 ppm represents the maximum concentration which was without significant effect after repeated 7-hour daily exposures.

RESULTS OF SINGLE EXPOSURES OF RATS TO THE VAPORS OF BROMOCHLOROMETHANE

Mortality from Single Exposure

The total number of rats used and the number that died from each exposure are listed in Table I and are summarized in Figure 1. Line AB of Figure 1 represents the exposure conditions causing total mortality. The maximum exposures causing essentially no mortality, line CD, were 0.1 hour at 40,000 ppm; 0.4 hour at 20,000 ppm; 1.5 hours at 10,000 ppm; and 7.0 hours at 5,000 ppm.

Drowsiness was apparent in rats exposed for 7.0 hours to 1,500 ppm and 5,000 ppm. Rats exposed to 10,000 ppm were very drowsy after

TABLE II

Summary of Single Vapor Exposures of Female Rats to Bromochloromethane (CH_2BrCl) to Determine Organic Injury

Calc. vapor conc. ppm	Dur. of Exp. in hours	No. of rats	Cont. Group	Average Body Weight, g		Average Organ Weights, g/100 g body weight					Histopathology	
				Before exposure	Starved	Lung	Heart	Liver	Kidney	Spleen	Liver	Kidney
0	0	8	Series A	145	138	0.76	0.43	3.08	0.83	0.43	N	N
0	0	10	Series B	142	134	0.85	0.47	3.36	0.90	0.47	N	N
0	0	10	Series C	149	140	0.81	0.46	2.92	0.86	0.26	N	N
40,000	0.1	4	A	138	131	0.82	0.49	3.76b	0.93b	0.38	+	N
40,000	0.05	4	A	140	138	0.88	0.47	3.52a	0.88	0.36	¼±	N
40,000	0.025	5	C	145	136	0.74	0.47	2.84	0.87	0.27	N	N
10,000	0.7	4	A	157	149	0.73	0.45	3.81b	0.91a	0.46	+	N
10,000	0.4	4	A	151	142	0.77	0.46	3.60b	0.91	0.61	±	N
10,000	0.2	4	A	147	138	0.86	0.47	3.38a	0.87	0.48	¾±	N
10,000	0.1	5	B	145	127	0.81	0.49	3.32	0.89	0.37	N	N
10,000	0.05	5	B	136	126	0.87	0.50	3.32	0.94	0.34	N	N
5,000	7.0	4	A	156	137	0.99	0.50	4.38c	1.01b	0.39	+	±
5,000	0.5	5	B	136	127	0.88	0.48	3.56	0.91	0.49	¼±	N
5,000	0.3	5	B	146	138	0.95	0.46	3.47	0.93	0.46	N	N
5,000	0.2	5	B	136	128	0.77	0.48	3.23	0.92	0.53	N	N
5,000	0.1	5	B	139	130	0.77	0.48	3.23	0.92	0.50	N	N
1,500	7.0	4	A	146	136	0.85	0.50	3.60a	0.91a	0.40	+	N
1,500	3.0	5	C	147	139	0.75	0.47	3.04	0.87	0.26	N	N
1,500	2.0	5	C	146	137	0.79	0.47	3.11	0.88	0.30	N	N
1,500	1.5	5	C	147	138	0.78	0.46	2.88	0.86	0.26	N	N
800	7.0	4	A	154	143	0.77	0.45	3.36	0.85	0.41	±	N
600	7.0	5	C	151	140	0.70	0.45	2.86	0.90	0.26	N	N

a = P = 0.01 to 0.05 b = P = 0.001 to 0.01 c = P = <0.001 N = Normal when compared to controls ± = Questionable response + = Very slight ++ Slight +++ Moderate ++++ Severe +++++ Very severe.

1½ hours and unconscious after two hours. Rats exposed to 20,000 ppm were unconscious at the end of 15 minutes exposure and those exposed to 40,000 ppm were unconscious after six minutes of exposure. Deaths generally occurred during exposure and appeared to be due entirely to anesthesia. With few exceptions, rats that recovered consciousness quickly regained any loss of body weight and delayed deaths were exceptional.

Organic Injury from Single Exposures

The results of the exposures to determine the most severe conditions resulting in no organic injury are summarized in Table II, and Figure 1. No significant gross pathological changes were seen. Microscopic evidence of organic injury was detected only in the liver although increases in organ weights were also seen in the kidney. The degree of injury was slight being characterized by very small vacuoles distributed throughout the parenchyma but not typical of fatty degeneration. Significant increases in liver weight often accompanied histopathological changes of this organ.

Line EF on Figure 1 represents the most severe conditions which did not cause detectable organic injury. The maximum exposures judged to be without detectable organic changes were 0.025 hour at 40,000 ppm; 0.1 hour at 10,000 ppm; 0.3 hour at 5,000 ppm; 3.0 hours at 1,500 ppm; and 7.0 hours at 600 ppm.

RESULTS OF REPEATED 7-HOUR DAILY EXPOSURES TO BROMOCHLOROMETHANE

1000 ppm (5.3 mg/liter) 79 to 82 Exposures in 114 Days

Male rats exposed to 1000 ppm were normal in appearance, activity and growth. Blood urea-nitrogen (BUN) values were within normal limits. Terminal inorganic blood bromide levels were high, 122 mg Br^-/100 ml (122 mg %). Although the organs all appeared normal at au-

topsy, changes were seen in the livers when they were examined microscopically. These were characterized by very slight proliferation of the bile duct epithelium with very slight portal fibrosis and inflammation. There was some cloudy swelling of the parenchymal cells in the midzonal areas spreading to the central areas of the lobule. Numerous parenchymal cells in the midzonal area and portal area contained many small vacuoles. There was an increase in the average liver and kidney weights of this group when compared to those of the controls.

The female rats exposed to 1000 ppm of bromochloromethane were normal in appearance and activity and their average body weight and growth were normal. Hematological values were within normal limits as were BUN levels. Fatty and enlarged livers were seen grossly when the rats were sacrificed. The average liver and kidney weights were elevated. Microscopically, pathological changes similar to those described for the male rats were seen with some portal fibrosis noted in the liver. Blood bromide levels were elevated, Table IV.

Male guinea pigs exposed to 1000 ppm of bromochloromethane were normal in appearance and growth. Average body weights were below the controls. The average liver and kidney weights were elevated, Table III. BUN values were normal and there were no gross pathological changes evident. Microscopically, however, decreased spermatogenesis was seen in the tu-

TABLE III

Summary of Terminal Average Body and Organ Weights of Animals Receiving Repeated 7-Hour Exposures to Bromochloromethane (CH_2BrCl) 5 Days per Week for Four to Six Months

Species	Sex	Group	Ratio of survival	Final average body weight, g	Organ Weights, g/100 g body weight					
					Lung	Heart	Liver	Kidney	Spleen	Testes
Guinea pig	M	Unexposed Control	8/10	750	0.73	0.30	3.47	0.68	0.14	0.46
	M	1000 ppm CH_2BrCl	8/10	609c	0.67	0.30	3.98b	0.76b	0.13	0.38
	M	500 ppm CH_2BrCl	8/10	624b	0.75	0.31	3.67a	0.71a	0.13	0.46
	F	Unexposed Control	8/10	690	0.80	0.28	3.82	0.66	0.16	
	F	1000 ppm CH_2BrCl	8/10	602bb	0.79	0.29	3.98a	0.75c	0.18	
	F	500 ppm CH_2BrCl	8/10	632a	0.74	0.29	3.98a	0.71	0.18	
Rabbit	M	Unexposed Control	2/2	3,235	0.38	0.20	2.52	0.44	0.04	0.16
	M	1000 ppm CH_2BrCl	2/2	3,275	0.40	0.20	3.28	0.46	0.04	0.08
	M	500 ppm CH_2BrCl	2/2	2,815	0.35	0.18	2.69	0.45	0.04	0.17
	F	Unexposed Control	2/2	3,205	0.36	0.20	2.44	0.38	0.04	
	F	1000 ppm CH_2BrCl	2/2	2,585	0.30	0.17	3.31	0.40	0.03	
	F	500 ppm CH_2BrCl	1/2	3,480	0.30	0.19	2.80	0.44	0.05	
Mouse	F	Unexposed Control	8/10	30	—	—	5.3	1.2	—	
	F	1000 ppm CH_2BrCl	8/10	27b	—	—	7.3d	1.5b	—	
	F	500 ppm CH_2BrCl	9/10	22d	—	—	6.4d	1.5d	—	
Rat	M	Unexposed Control	19/20	341	0.55	0.31	2.46	0.68	0.29	0.87
	M	1000 ppm CH_2BrCl	17/20	306	0.56	0.32	3.20d	0.75d	0.32	0.85
	M	500 ppm CH_2BrCl	17/20	300	0.56	0.34	2.77d	0.69	0.32	0.82
	F	Unexposed Control	17/20	203	0.73	0.37	2.67	0.71	0.36	
	F	1000 ppm CH_2BrCl	19/20	206	0.70	0.38	3.65d	0.82d	0.35	
	F	500 ppm CH_2BrCl	19/20	210	0.70	0.38	3.05d	0.75	0.38	
	F	Unexposed Control	12/12	215	0.64	0.39	2.70	0.76	0.28	
	F	Air Exposed Control	12/12	220	0.64	0.34	2.77	0.75	0.32	
	F	370 ppm CH_2BrCl	9/10	232	0.63	0.38	2.98bb	0.78	0.25	
Dog	M	Unexposed Control	1/1	14,100	0.78	0.67	2.66	0.42	0.16	0.17
	M	Air Exposed Control	1/1	11,300	0.86	0.98	2.65	0.44	0.25	0.19
	M	370 ppm CH_2BrCl	1/1	12,800	1.08	0.98	3.03	0.48	0.27	0.13
	F	Unexposed Control	1/1	11,000	0.76	0.81	2.31	0.41	0.21	
	F	Air Exposed Control	1/1	12,200	1.08	0.91	2.43	0.37	0.36	
	F	370 ppm CH_2BrCl	1/1	9,300	1.08	0.99	2.90	0.49	0.46	

Probability values (P) a = $P > 0.05$ b = $P = 0.01$–0.05 bb = $P \leq 0.045$ c = $P = 0.001$–0.01 d = $P < 0.001$.

TABLE IV

Summary of Average Blood Bromide, Blood Urea-Nitrogen and Blood Non-Protein-Nitrogen Levels in Animals Exposed Repeatedly to the Vapors of Bromochloromethane in Air

Species	Sex	Months on exposure, day bled	Vapor conc. ppm	Blood Bromide			Blood Nitrogen		
				No. of animals	mg Br^-/100 ml	Analytical method*	No. of animals	Urea N mg/100 ml	Total NPN mg/100 ml
Guinea pig	M	4 Tues.	0	2	5.2	W	2	20.8	
	M	4 Tues.	1000	3	38	W	2	16.7	
	M	4 Tues.	500	3	33	W	2	18.1	
	F	4 Tues.	0	3	4.8	W	2	26.0	
	F	4 Tues.	1000	3	44	W	2	23.0	
	F	4 Tues.	500	3	43	W	2	24.8	
Rabbit	M	4 Wed.	0	2	5	W	2	20.5	
	M	4 Wed.	1000	2	67	W	2	15.3	
	M	4 Wed.	500	2	50	W	2	16.5	
	F	4 Wed.	0	2	5	W	1	30.7	
	F	4 Wed.	1000	2	67	W	2	22.2	
	F	4 Wed.	500	1	60	W	1	21.4	
Rat	M	4 Thurs.	0	3	8	W	2	14.8	
	M	4 Thurs.	1000	3	122	W	2	13.9	
	M	4 Thurs.	500	3	88	W	2	16.0	
	F	4 Fri.	0	3	5	W	2	15.2	
	F	4 Fri.	1000	3	122	W	2	15.9	
	F	4 Fri.	500	3	83	W	2	18.7	
	F	6 Wed.	0	3	0.9	S	8	20.8	48
	F	6 Wed.	370	3	73	S	3	12.9	47
Dog	M	3½ Wed.	0	1	3.9	W			
	M	5 Thurs.	0	1	0.0	S			
	M	6 Tues.	0	2	0.9	S	2	21.8	45
	M	3½ Wed.	370	1	22	W			
	M	5 Thurs.	370	1	39	S			
	M	6 Thurs.	370	1	41	S	1	30.5	40
	F	3½ Wed.	0	1	2.7	W			
	F	5 Thurs.	0	1	0.0	S			
	F	6 Tues.	0	2	0.7	S	2	21.6	55
	F	3½ Wed.	370	1	60	W			
	F	5 Thurs.	370	1	25	S			
	F	6 Tues.	370	1	31	S	1	13.7	40

* Analytical method for blood bromide
W Wuth's Hepler, O. E., Manual of Clinical Laboratory Methods, Charles C Thomas, Springfield, Illinois, 1951
S Shrader's Shrader, S. A., *et al.*, *Ind. Eng. Chem. Anal. Ed. 14:* 1 (1942)

bules of the testes with fibrosis in numerous tubules and only the germinal epithelium remaining in other tubules.

Female guinea pigs exposed to 1000 ppm were normal in appearance and activity. Body weights were below those of the controls but within normal limits for animals of their age. BUN values were within normal limits. An increased number of leucocytes was seen; primarily neutrophils. There was no evidence of pathological changes either grossly or microscopically. Organ weights were normal when compared to the controls.

Female mice exposed to 1000 ppm were normal in appearance and growth. No evidence of pathological changes due to the compound was seen either grossly or microscopically. There was a slight increase in the average liver and kidney weights when compared to those of the controls.

Male rabbits exposed to 1000 ppm of bromochloromethane were normal in growth, appearance and activity. BUN values were within normal limits. Blood bromide levels were elevated, Table IV. There was no evidence of gross pathological change noted at autopsy. Histopathological examination of the tissues revealed testicular changes characterized by decreased spermatogenesis with replacement fibrosis occurring in the tubules of one of the rabbits. Histopathology of the other rabbit was normal. There was an apparent increase in the liver weight but the small number of animals makes it difficult to be certain of the significance of this finding.

Female rabbits exposed to 1000 ppm of bromochloromethane were normal when judged on the basis of appearance, growth, mortality, BUN, and gross and microscopic pathology. There was, however, an apparent increase in liver weight, Table III, and blood bromide levels were elevated, Table IV.

500 ppm (2.65 mg/liter) 79 to 82 Exposures in 114 Days

Male rats exposed to 500 ppm were normal when judged on the basis of mortality, growth, activity, appearance, BUN and gross and microscopic pathology. All organ weights were normal with the exception of a small increase in weight of the liver. Although the difference in average liver weights was small (2.77 vs. 2.46) almost all rats were affected as indicated by the highly significant P value. Since no pathological changes were seen it probably indicates that the organ was under only slight stress. Blood bromide ion levels averaged 58 mg % while the controls averaged an 8 mg %.

Female rats were normal when judged on the basis of mortality, growth, appearance, BUN, hematology and gross pathology. However, blood bromide levels were elevated, Table IV, the average liver weight was high, and there were slight pathological changes as shown by bile duct epithelial proliferations and very slight portal fibrosis, together with occasional large and small vacuoles in parenchymal cells of the midzonal areas.

Male and female guinea pigs and rabbits exposed to 500 ppm were judged normal in all respects except for elevated blood bromide levels, Table IV.

TABLE V

Average Terminal Hematological Values for Animals Receiving Repeated 7-Hour Exposures to 500 and 1000 ppm Bromochloromethane 5 Days/Week for Four Months

Species	Treatment	Sex	No. of animals	RBC × 10^6	WBC × 10^3	Differential Count (%)			
						Neutrophils	Lymphocytes	Monocytes	Eosinophils
Rat	Unexposed control	F	5	8.8	16.9	14.2	82.9	0.4	3.0
	1000 ppm	F	10	8.7	14.4	18.9	79.5	1.0	1.5
Guinea pig	Unexposed control	F	3	5.5	10.1	11.0	87.7	0.3	1.0
	1000 ppm	F	3	5.5	15.4	29.3	65.0	0.0	5.7
	500 ppm	F	3	5.3	13.4	9.0	90.3	0.0	0.7

Female mice exposed to 500 ppm of bromochloromethane were low in average body weight. This was not considered to be of significance since the group exposed to 1000 ppm was normal in body weight. Because of the low body weights, a comparison of the liver and kidney weights with those of the controls has little meaning. The mice were normal in all other respects including gross and microscopic pathology.

370 ppm (1.96 mg/liter) 135 Exposures in 195 Days

Female rats exposed to 370 ppm of bromochloromethane were normal when judged on the basis of mortality, growth, activity, appearance, gross and microscopic pathology, BUN and NPN levels, and a statistical comparison of organ weights. However, the average liver weight was still higher than the controls ($P = 0.045$) indicating the possibility that the rats were still under stress. Blood bromide levels were elevated, Table IV.

The male and female dogs exposed to 370 ppm of bromochloromethane were normal in appearance, activity and growth, BUN, NPN, and hematological values were within the normal limits. Blood bromide levels were elevated, Table IV. The data does not permit judging whether the bromide levels had actually reached a maximum.

130 ppm (0.69 mg/liter) 45 Exposures in 66 Days

The 4 rabbits exposed 7-hours per day five days per week to an average concentration of 130 ppm (by analysis) grew normally and appeared active and healthy despite the large number of cardiac punctures they received. The results of the determination of the bromide ion concentration in the blood and serum are listed in Table VII. As can be seen in Table VII, the samples were taken before exposure and immediately after exposure in order to sample the lowest and highest blood concentrations. After the first week, samples were generally taken on Friday afternoon and Monday morning.

The results of the analyses indicate that the blood bromide ion concentration had reached a maximum by the end of the second week and were of the order of 30–35 mg % Br^- on Friday afternoon.

The comparison of results of the gold chloride analysis with that of the ashing technique are reported in Table VIII. All values have been converted to bromide ion to facilitate comparison.

TABLE VI

Average Hematological Values for Dogs Receiving Repeated 7-Hour Exposures to 370 ppm Bromochloromethane Five Days per Week for Six Months

Treatment	When sampled	Sex	No. of animals	WBC $\times 10^3$	Hb g/100 ml	Hematocrit	Neutrophils	Lymphocytes	Monocytes	Eosinophils	Basophils
							%	%	%	%	%
370 ppm CH_2BrCl	Preexposure	M	1	15.2	11	42	57	41	2	0	0
	Terminal	M	1	12.8	14.5	54	69	21	5	5	0
Air exposed control	Preexposure	M	1	10.1	12.0	42	42	52	4	2	0
	Terminal	M	1	10.3	14.0	51.5	48	49	1	2	0
Unexposed control	Preexposure	M	1	21.4	13.0	44.5	57	42	0	1	0
	Terminal	M	1	15.8	13.8	50	49	45	1	5	0
370 ppm CH_2BrCl	Preexposure	F	1	16.1	12.0	46	61	34	2	3	0
	Terminal	F	1	10.0	14.0	49	49	45	3	1	0
Air exposed control	Preexposure	F	1	19.4	11.0	38	32	47	1	0	0
	Terminal	F	1	14.8	14.5	49	56	38	3	3	0
Unexposed control	Preexposure	F	1	22.9	14.0	45	48	46	3	3	0
	Terminal	F	1	16.7	13.0	47	52	43	3	2	0

Significance of Results

Bromochloromethane was shown to have very little capacity to cause liver injury from single or repeated exposures. Deaths from acute vapor exposures were anesthetic in nature and unless death occurred from anesthesia, complete recovery generally occurred. The low hepatotoxicity found in this study confirms the conclusion of other investigators. However, this study failed to show the delayed deaths reported by Comstock,[6] Svirbely,[2] and Highman[3]. Comstock attributed the delayed deaths to edema in the lungs but the study reported by Svirbley and Highman indicated only slight pneumonitis in mice, rats and guinea pigs. The apparent discrepancy between the present data and that of Svirbely and Highman may be due to a difference in response in mice and rats since these workers concluded that rats showed less pathological changes than mice. Svirbely and Highman did not indicate whether delayed deaths occurred with rats or guinea pigs. No explanation of the discrepancy in response between the present data and that of Comstock is readily apparent. Possibly the delayed deaths they reported resulted from secondary infection in the lungs due to the exposure. The data presented herein does not agree with the limited data published by Comstock *et al.*[5] who concluded that rats could survive 15 minutes exposure to 54,000 ppm.

Although the present data is in essential agreement with that published by Underwriters' Laboratories,[4] it does not support their conclusion that bromochloromethane and carbon tetrachloride are equal in toxicity. The difference in conclusions is no doubt due to the limited data of the Underwriters' experiment. Figure 2, which compares bromochloromethane with carbon tetrachloride, indicates the hazards of comparing the vapor toxicity of two materials at one or two concentrations and time intervals such as has

TABLE VII

Summary of Inorganic Whole Blood Bromide Levels in Rabbits Receiving Repeated 7-Hour Daily Exposures to 130 ppm Bromochloromethane 5-Days per Week

Number of exposures	No. of days	Day	Time	Blood Bromide Ion mg/100 ml				
				Rabbit Number				
				101	102	106	107	Ave.
0	0	Wed.	PM	0.32	0.30	0.13	0.26	0.25
1	0	Mon.	PM	7.1	7.3	6.8	8.6	7.45
1	1	Tues.	AM	5.9	6.0	7.3	6.8	6.5
2	1	Tues.	PM	12.6	13.8	14.0	14.6	13.8
2	3	Wed.	AM	11.3	10.8	10.9	12.6	11.4
5	4	Fri.	PM	29.4	26.5	27.2	27.9	27.8
5	7	Mon.	AM	17.3	17.3	18.3	16.9	17.5
10	12	Fri.	PM	31.6	34.0	35.1	35.6	34.1
10	14	Mon.	AM	18.8	17.3	19.2	16.6	18.0
14	18	Fri.	AM	25.7	—	27.0	28.7	27.1
15	21	Mon.	AM	21.6(44)	16.3(35)	20.8(45)	19.0(45)	19.4(42)
45	63	Fri.	PM	17.6	33.3	32.0	41	31.3
45	66	Mon.	AM	34.8	23.1	34.4	25.6	29.5
45	88	Tues.	AM	7.7	2.0	8.7	1.9	5.1
45	122	Mon.	AM	1.0	0.66	0.85	0.71	0.8

Values in parenthesis were determined by a gold chloride method and represent mg NaBr/100 ml of serum.

TABLE VIII

Milligrams Br^-/100 ml (mg %) in Rabbit Serum and Blood 21 Hours after Oral Intubation of Sodium Bromide

Dosage in g/kilogram of body weight	Determined in	2.0		1.0		0.5		0.0	
Rabbit Number		1	2	3	4	5	6	7	8
Medical Laboratory A (gold chloride method)	Serum	Too high for method	293	179	191	94	100	1.6	3.9
Medical Laboratory B (gold chloride method)	Serum	294	—	168	—	96	—	1.6	—
Chemical Laboratory (ashing method)	Serum	291	272	175	175	Lost	92	0.2	0.2
Chemical Laboratory (ashing method)	Whole blood	178	207	127	145	67	70	0.4	0.6

All values are the average of two determinations and have been converted to mg Br^-/100 ml.

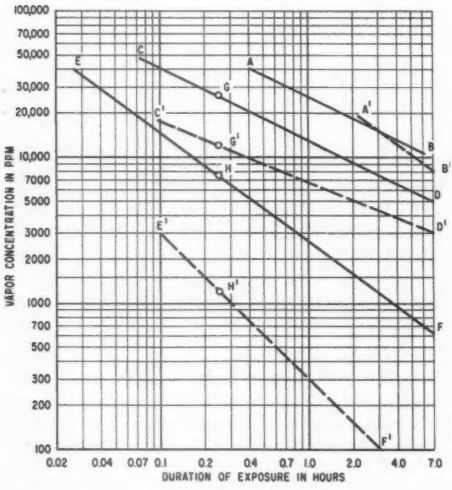

FIGURE 2. Comparison of the Vapor Toxicity of Bromochloromethane and Carbon Tetrachloride. The solid lines pertain to bromochloromethane, the broken lines to carbon tetrachloride. Lines AB and A'B' represent minimum exposure intensities resulting in essentially total mortality. Lines CD and C'D' represent the maximum exposure intensities resulting in essentially no mortality. Lines EF and E'F' represent the maximum exposures resulting in no organic injury.

been done in limited studies. For example, if compared only on the basis of exposures causing essentially total mortality, as was done by Underwriters', the two compounds are essentially equal. However, it is obvious that when compared on the basis of maximum exposures causing no deaths or no organic injury, which are more valid criteria where hazards to human life are concerned, there is a large advantage in favor of bromochloromethane. For example, considering 0.25 hour exposures, more than 26,000 ppm, point G, of bromochloromethane, were required before it was lethal to any of the rats so exposed, while concentrations of over 12,000 ppm, point G', of carbon tetrachloride were found to be lethal. The difference between exposures causing no detectable organic injury is even more striking. Again considering a 0.25 hour exposure, 7500 ppm, point H, bromochloromethane and 1200 ppm of carbon tetrachloride, point H', are the maximum concentrations which did not cause detectable organic injury.

Figure 2 does not indicate another major difference between bromochloromethane and carbon tetrachloride, the difference in the type of pathological change which was found to result from excessive exposure. The injury to the liver due to exposure of bromochloromethane was limited to reversible fatty changes wereas the changes due to carbon tetrachloride were permanent.

The results of repeated vapor exposures indicate that bromochloromethane has a low chronic vapor toxicity. Repeated exposure to a vapor concentration of 370 ppm was without significant effect. However, an increase in liver weight without pathological changes occurred in female rats and may indicate a stress on that organ. No apparent serious injury occurred even at 1000 ppm. No reason is readily apparent for the difference in response of animals exposed to 1000 ppm reported by Svirbely and that described in this report.

Blood Bromide Concentrations

Tables IV, VII, and VIII summarize the results of the blood and serum bromide determinations made during this study. It is of interest to compare the results of the samples analyzed by

the gold chloride method as well as the ashing technique, Table VIII. It would appear from inspection that there is reasonable agreement between the two methods. However, the writers experienced considerable difficulty in reconciling the original results reported by the three laboratories although all three laboratories reported their results in terms of milligrams bromide per 100 ml of blood (mg %). After investigation, it was found that the results of analysis by the gold chloride method actually were in terms of milligrams of sodium bromide per 100 ml not mg of bromide as common medical usage would imply. When the correction factor of 79.9/102.9 or 0.78 was applied the reasonable agreement resulted. Hence, considerable caution must be exercised in using the blood bromide levels reported in the literature. Not only does the previously mentioned difference occur but a factor must also be applied to convert whole blood bromide concentrations with blood serum bromide concentrations. On the basis of this limited study a factor of 0.7 appears proper.

Hence, if it is necessary to convert from the values (mg NaBr/100 ml) reported by the gold chloride technique to the bromide ion concentration in whole blood, it is necessary to multiply by 0.78 × 0.7 or 0.55. This is the relationship found in the rabbits exposed to 135 ppm of bromochloromethane, Table VII, and confirms previous experience in this laboratory. All values listed in this report have been converted to Br^- unless specifically stated as otherwise.

In animals exposed to 370 ppm of bromochloromethane for six months, terminal blood bromide ion levels of 44–73 mg/100 ml (mg %) were determined. Although this level represents a large increase in bromide ion, no adverse effects typical of bromism (apathy, obesity, and inactivity) were noted at this or higher levels (up to 122 mg % Br^-) reported in this study. The rabbits which received 7-hour daily exposures to 135 ppm quickly (two weeks) reached a maximum blood bromide ion level of 30–34 mg %. On the basis of the data it appears that exposures to 200 ppm would result in bromide ion concentrations at about 40 mg %. Svirbely[2] reported no adverse effects in dogs with levels as high as 220–260 mg % Br^-. The analytical method used by Svirbely would probably give results comparable to those of Shrader used in this study.

The literature has very little uniformity of opinion concerning what chronic blood bromide levels are associated with bromism. Perhaps some of the best data is that of Rosenblum[13] who fed dogs for one year on diets either fumigated with methyl bromide or high in sodium bromide. He concluded that Br^- levels of 176–192 mg % (22–24 meq/liter) were accompanied by no adverse effects, while a level of 272 mg % (34 meq/liter) was found in animals adversely affected. Rosemblum used the Brodie and Friedman[14] method of analysis for bromide. It is evident that blood bromide levels reported in this study are well below those considered safe by Rosenblum.

Industrial Hygiene Standard

The data presented indicate that little likelihood of organic injury is present if repeated 7-hour daily exposures are limited to 400 ppm or less. However, since the blood bromide levels were found to be rather high in animals exposed to this concentration and since it is possible that other chemicals or medicinals may be contributing bromide, it is recommended that the time-weighted average of all exposure not exceed 200 ppm.

Precautions for Safe Handling

Ingestion

There should be no hazard from swallowing in ordinary industrial operations. However, the swallowing of substantial quantities, such as might occur accidentally or willfully, could result in injury. Containers should be properly labeled so that ingestion due to mistaken identity cannot occur. The material should be kept out of the reach of children.

Eye Contact

It is advisable to protect the eyes where likelihood of contact with the liquid exists. Safety glasses, preferably with side shields, or a face shield are recommended to prevent the pain and discomfort resulting from getting the material in the eyes. If the material gets into the eyes, they should be flushed thoroughly with large amounts of water and medical attention should be obtained.

Skin Contact

Although it causes an unpleasant stinging sensation on the skin, this material presents no practical hazard from the standpoint of irritation or skin absorption and can be expected to cause dermatitis only in instances where exposure is extensive (prolonged or frequently repeated). Prolonged contact with contaminated clothing should be avoided. If substantial quantities are spilled on the person, contaminated shoes and clothing should be removed promptly and not worn again until free of all the material.

Vapor Inhalation

The primary hazard from inhalation of the vapors is that due to anesthesia, the likelihood

of organic injury being remote. If it is necessary to use in a small or confined space, do not remain in the area. If a person should show ill effects from breathing the vapors, he should go or be removed to fresh air at once. If overcome by the vapors, the individual should be removed to fresh air and medical attention should be given. If breathing stops, artificial respiration should be administered.

The vapor concentration in the work room air where repeated human exposure is likely should be maintained below 400 ppm, with a time-weighted average for exposures not to exceed 200 ppm.

Summary

Bromochloromethane (CH_2BrCl) has been shown to be an effective fire extinguishing agent and it has therefore been considered as a replacement for carbon tetrachloride. Extensive studies using laboratory animals have been conducted to determine the acute and chronic vapor toxicity of this material. The material was found to cause a rather prolonged anesthesia at high concentrations and this was shown to be the cause of death in acute exposures. The material has only a slight capacity to cause liver injury and if such should occur, it is apparently reversible in nature as contrasted to the fibrotic changes resulting from much less severe exposure to carbon tetrachloride.

Single exposures of various intensities were given to matched groups of rats in order to establish the exposure intensities resulting in essentially complete mortality; complete survival; and in no detectable organic injury.

Repeated 7-hour daily exposures for four months of rats, rabbits, guinea pigs and mice to 1000 ppm resulted in adverse effects in all species whereas exposures to 500 ppm caused only minor responses, these being limited to female rats. After six months of repeated 7-hour daily exposures to an average concentration of 370 ppm no effects of consequence were seen in a group of 20 female rats or in one male and one female dog. Blood bromide levels are reported for several species and for several exposure intensities.

The standard for evaluating regular 7- to 8-hour daily exposures may be defined as the concentration below which practically all analytical results must fall. The value of 400 ppm is suggested as this standard for bromochloromethane, with a time-weighted average for all exposures not to exceed 200 ppm.

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Separation of Fluoride by Ion Exchange: Application to Urine Analysis

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URINARY fluoride concentrations have been shown by Collings, *et al.*[1, 2] to reflect exposures to particulate and gaseous inorganic fluorides. Use of urinary excretion levels to indicate excessive inhalation of fluorides has been hampered by cost and time considerations when the determination of fluoride has, of necessity, been preceded by a Willard and Winter[3] distillation for isolation of the fluoride.

The two procedures reported here are the summations of initial investigations into the feasibility of the ion exchange process for the separation of fluoride, not only from the inorganic constituents of urine, but from the organic as well. The first ion exchange procedure, preliminarily reported,[4] has as its basis the adsorption of fluoride on the hydroxide form of anionic resin and the differential elution of the fluoride with 0.3*M* sodium hydroxide. The second approach, subsequently pursued by one of us (N.A.T.) in an effort to further simplify the analysis, depends upon the formation of the fluoberyllate ion[5] for the elution of fluoride from a column of the acetate form of anionic resin.

The ion exchange separations require minimal laboratory facilities and, by self-regulating operations, transpose the fluoride to media suitable for direct spectrophotometric determination by the methods of Megregian[6] and of Bellack and Schouboe.[7] Either ion exchange method has applicability to air analysis in addition to the more stringent requirements of urine analysis.

Melvin, Yeager, and Cholak[8, 9] successfully applied the anionic resin, Duolite A-41, in the acetate form to the isolation of fluoride from blood serum in a manner similar to that reported by Nielsen[10] for the concentration of fluoride in Willard and Winter distillates and in aqueous solutions of air-borne fluorides. Extensive efforts on our own part to elute the fluoride from acetate columns with sodium acetate failed to achieve complete separation from the interferences occurring in urine.

Zipkin, Armstrong, and Singer[11] had shown that the hydroxide form of Dowex 1 was highly effective in separating fluoride from the phosphate ion. Our trials indicated that a somewhat greater reduction of interferences could be obtained with the hydroxide form than with the acetate when applied to urine and that residual interferences could be adequately suppressed by pretreatment of the urine with cationic resin and activated carbon.

Notwithstanding unfavorable experiences with the acetate form of anionic resin, this form proved to be appropriate when beryllium ion was substituted for acetate ion as the eluting agent.

The ion exchange procedures require that the urine specimens be free of sediments capable of entraining fluorides. Bacteriostatic agents such as thymol and chloroform, commonly used as urine preservatives, do not adequately prevent precipitation of alkaline-earth salts. EDTA (ethylenediaminetetraacetic acid) had been suggested by Nelson[12] as a preservative in the analysis of urine for heavy metals and had also been used effectively by Newman[13] to complex interfering cations in the ion exchange separation of fluoride from phosphate rock. It appeared that both functions of EDTA would be useful in the separation of fluoride from urine. When EDTA was used in conjunction with hydroxide resin, consistently low recoveries of urinary fluorides were obtained, but no appreciable losses were evident when EDTA preserved urine was processed by beryllium elution from acetate resin.

A second technique investigated for preserving urine specimens involved the addition of dry cationic resin in the free acid form to the urine. The urine was thus pickled without increasing the total ionic content. This method of preservation proved compatible with the adsorption of fluoride by both hydroxide and acetate resins.

Ion Exchange Apparatus and Reagents

The rate of flow through the ion exchange resin beds was not critical in the present work and was more conveniently held from 5 to 10

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drops per minute by the selection of resin particle-size and column diameter rather than by recourse to more elaborate arrangements, often specified, which involve stopcocks and constant-level devices. Capillary forces were found strong enough to prevent air from being drawn into the resin beds, even on several days standing, provided that only loose-fitting caps were used for covering the reservoirs or columns.

Glass wool plugs, while seemingly the logical choice to prevent disturbance of the surface of the resin beds, caused such difficulties as channeling, air-locks, and variable hold-up of liquid. Crushed quartz, also, was not suitable because the interlocking effect of the angular particles prevented free expansion and contraction of the resins. None of these difficulties were experienced when a layer of quartz sand was used for protection of the resin surface.

Chromatographic tubes, 10 mm ID × 300 mm (Corning Cat. No. 38450), were used for the ion exchange separations. Reservoirs were constructed from 125-ml, pear-shaped, Squibb separatory funnels by sealing 3-cm lengths of 10 mm ID glass tubing in place of the stopcocks. The reservoirs were attached to the tops of the chromatographic tubes with 4-cm lengths of ⅜-inch ID gum rubber tubing and the assemblies were supported in a separatory-funnel rack.

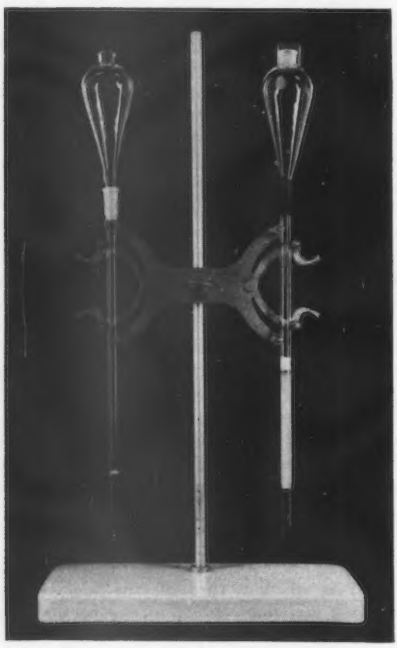

FIGURE 1. Ion Exchange Apparatus.

An all-glass assembly was also devised. A 14/35 standard taper male joint was sealed to the bottom of a 125-ml, Squibb separatory funnel blank and a matching female joint was sealed to the top of the chromatographic tube (Corning Cat. No. 38450). Chromatographic tubes of smaller diameter unnecessarily restrict the flow rate of solutions and should not be used in place of the 10 mm ID tube. The two assemblies are shown in Figure 1.

Resins were purified in a large chromatographic tube (80 mm × 330 mm).

Dowex 50W-X8, 20 to 50 mesh, in the free acid form, was used as sample preservative in the first procedure. The resin was washed in the large column with distilled water followed by a volume of 3*M* hydrochloric acid equal to five times the wet resin volume and finally with distilled water until the effluent was neutral to pH test paper. During the washing, the flow rate was restricted with a pinch clamp. Excess water was drawn from the resin bed by suction and the resin air-dried in a glass tray at 40°C.

Dowex 50W-X8, 100 to 200 mesh, in the free acid form, and Dowex 1-X8, 100 to 200 mesh, in the chloride form, were sieved as a thin slurry in a flow of distilled water through 60 and 200 mesh sieves. The resin particles retained by the 200 mesh sieve were purified with consecutive washes of three volumes of 95 per cent ethanol, water, five volumes of 3*M* hydrochloric acid, and water to neutrality. The purified resins were stored as a slurry in distilled water. Before use, the water above the settled resin was adjusted to a volume equal to the volume occupied by the wet resin. For routine use, removal of fines by repeated decantations replaced sieving.

Acid-washed, activated coconut charcoal, 50–100 mesh, (Barneby-Cheney Co.) was digested for several hours at 100°C as a thick slurry in 20 per cent sodium hydroxide. The charcoal was then rinsed in a column with distilled water followed by five volumes of 3*M* hydrochloric acid and by water until neutral to pH test paper. A 1:1 slurry was prepared by allowing a suspension in water to settle and adjusting the supernatant water to a volume equal to that occupied by the wet carbon.

White quartz sand, 60 to 120 mesh, purified by digestions at 100°C with 20 per cent sodium hydroxide and 1:3 hydrochloric acid, was used as a protective layer over the resin beds.

Sodium hydroxide solutions, 3*M*, for conversion of anionic resin to the hydroxide form and 0.3*M* for elution of fluoride, were prepared from a special, low-carbonate analytical-grade product or from a 50:50 solution by weight from which the sodium carbonate had been allowed to settle.

Disodium ethylenediaminetetraacetate (Se-

questrene NA2 3X, Alrose Chem. Co.) was used in solid form as sample preservative in the second procedure.

Sodium acetate solution, 1*M*, for conversion of anionic resin to the acetate form, was prepared from analytical grade, fused product.

Acetic acid, 0.1*M*.

Beryllium stock solution, 1.0*M* with respect to acetic acid and 0.05*M* with respect to beryllium nitrate or acetate. Preference was given to solutions containing the beryllium as acetate. These were prepared from beryllium carbonate (A. D. Mackay). The carbonate was analyzed for beryllium content by ignition to the oxide and a quantity of the carbonate containing 0.05 mole of beryllium was dissolved in 1.1 mole of glacial acetic acid with mild application of heat. Upon dilution to one liter with water, an opalescent solution was obtained which clarified spontaneously within a few days. (Note: Beryllium compounds are potentially injurious. Precautions should be taken to avoid inhalation of dust or spray.)

Beryllium Eluting Reagent, 0.1*M* with respect to acetic acid and 0.005*M* with respect to beryllium. This is a tenfold dilution of the beryllium stock solution.

Photometric Determinations

The methods of Megregian[6] and of Bellack and Schouboe[7] were found suitable for the final colorimetric determinations of the separated fluoride. The two methods are similar except for the dye used. Megregian's reagent is the more sensitive of the two but requires a narrow bandpass spectrophotometer. The reagent specified by Bellack and Schouboe is the more stable and may be used with filter photometers. Both methods are temperature sensitive and, because they depend upon the bleaching of a deep color, they require precisely matched cuvettes and accurate measurement of the color-forming reagent.

Megregian Dye Solution. Eriochrome Cyanine R (Geigy Co., Inc.) (1.800 grams per liter of aqueous solution).

Bellack and Schouboe Dye Solution. 4,5-dihydroxy-3-(p-sulfophenylazo)-2,7-naphthalenedisulfonic acid trisodium salt (Eastman Organic Chemicals, No. 7309) (1.916 grams per liter of aqueous solution).

Zirconium Reagent I (modified for use in determining fluoride in 0.3*M* sodium hydroxide medium). A solution of 0.265 gram of zirconyl chloride octahydrate in 50 ml of water was made up to one liter with concentrated hydrochloric acid (Sp. Gr. 1.19).

Zirconium Reagent II (for use in determining fluoride in 0.1*M* acetic acid medium containing beryllium). A solution of 0.265 gram of zirconyl chloride octahydrate in 50 ml of water was acidified with 700 ml of concentrated hydrochloric acid (Sp. Gr. 1.19) and then diluted to one liter with distilled water.

Mixed Color Reagent. Equal volumes of the selected dye solution and of the appropriate zirconium reagent were mixed to provide an amount required by the samples on hand.

Reference Solution. Ten milliliters of the appropriate dye solution (not the Mixed Color Reagent) were added to 100 ml of distilled water and then mixed with a solution prepared by diluting 7 ml of concentrated hydrochloric acid to 10 ml with distilled water. This reference solution was used only for obtaining the initial zero absorbance setting of the photometer. Thereafter, a zero fluoride standard was used as a reference inasmuch as it provided compensation for ambient temperature. The zero standard, as well as the samples, could not be exposed to the heat of the photometer longer than a few seconds without causing significant drift of the readings.

Colors were developed in the samples by adding exactly 5 ml of the Mixed Color Reagent to each of the 25-ml fractions obtained from the ion exchange columns. The samples were mixed thoroughly and allowed to stand long enough to come to temperature equilibrium (about one hour).

Standard fluoride solutions for preparation of curves were made up in media to match those of the samples by use of appropriate amounts of the more concentrated, stock eluting reagents. Curves obtained in the present work were linear to a concentration of 25 micrograms of fluoride per 25 ml of sample (30 ml of final solution) but were useful to 35 or 40 micrograms.

The data reported here were obtained with a Beckman Model DU spectrophotometer using closely matched, 22-mm, Kimble glass test tubes in a test tube adapter.[14] Colors which were developed with the Megregian Dye Solution were read at 536 millimicrons. When the Bellack and Schouboe Dye Solution was used, the colors were read at 580 millimicrons.

Separation Procedure I

ELUTION OF FLUORIDE FROM HYDROXIDE RESIN WITH HYDROXIDE ION

Preservation of Samples

Urine specimens should be collected in, or aliquots immediately transferred to, polyethylene bottles containing a 5-ml volume of dry, 20 to 50 mesh Dowex 50W for each 100 ml of urine.

Pretreatment of Samples

The pretreatment column consists of activated carbon at the bottom of the tube and Dowex 50W at the top, each occupying a l[illegible]ume, and is prepared as follows: Add a fe[illegible]ers of water to the chromatographic tube [illegible]en rapidly transfer a 1:1 slurry of 50 to 10[illegible] mesh activated charcoal to the tube by means of a 20-ml pipette whose tip has been cut off. When all except a few milliliters of the [illegible]ater has drained, add 20 ml of a 1:1 slurry of 100 to 200 mesh Dowex 50W. When the resin has settled but water has not completely drained, add enough dry, 60 to 120 mesh sand to make a layer about 2 cm thick.

Dilute 25 ml of the preserved urine to 250 ml in a volumetric flask. Pass 50 ml of the diluted urine through the pretreatment column to flush out the water. Discard the effluent. Then, pass the remaining 200 ml through the column and collect the effluent in a 6-oz. polyethylene bottle.

Separation of Fluoride

Prepare the separation column by adding a few milliliters of water to the chromatographic tube and then a 20-ml volume of a 1:1 slurry of 100 to 200 mesh Dowex 1. Twirl the tube before water has drained to level the surface of the resin bed and to dislodge resin particles adhering to the glass surfaces. Also, before the water has completely drained, add dry sand to a 2-cm depth.

Convert the resin to the hydroxide form by passing not less than 150 ml of 3*M* sodium hydroxide through the column and wash the resin bed with several portions of water until the effluent is neutral to pH test paper.

Pass 25 ml of the diluted and clarified urine through the column and wash with a few milliliters of water. Estimate the percentage of resin capacity used, as evidenced by a change in color of the resin, and pass an additional volume of urine through the column to approach, but not exceed, 15 per cent of the total resin capacity.

Rinse the resin bed with several portions of water totaling at least 50 ml and allow the columns to stand overnight before elution of the fluoride.

Flush the water from the resin bed with 10 ml of 0.3*M* sodium hydroxide and then elute the fluoride with precisely measured, 25-ml volumes of 0.3*M* sodium hydroxide. Collect five fractions and determine fluoride in each separately. The bulk of the fluoride should appear in the second, third or fourth fraction.

Experimental

Dowex 50W-X8, 20 to 50 mesh, in the free acid form was selected for trials as a urine preservative. Mold growth and precipitation of salts were adequately inhibited whether 2, 4, 8, or 10 ml of the air-dried resin beads per 100 ml of urine were used. Recoveries of fluoride (2.5 mg per liter of urine) ranged from 91.6% to 95.2% but did not correlate with the amount of resin. Recoveries of fluoride were in this range whether the resin was purified by a water wash alone or by a wash with 3*M* hydrochloric acid preceded and followed by a water wash.

The moisture content of the air-dried resin, determined as 13%, would be expected to cause an apparent fluoride loss of about 0.5% when the recommended quantity of 5 ml per 100 ml of urine is used.

Because of the acidity of the urine samples preserved with cationic resin, polyethylene bottles were used in preference to glass to avoid losses of fluoride by adsorption.

Preliminary experiments showed that the cationic resin, used as preservative, and anionic resin in the hydroxide form did not adequately suppress all interferences, but that activated carbon was effective in removing the residual interferences. A series of columns was prepared in order to determine the most effective combination of cationic resin and activated carbon for pretreatment of the preserved samples before their introduction to the anionic column. The results obtained with this series are shown in Table I. Obviously the urine must percolate first through the cationic resin and then through the activated carbon for maximal reduction of interferences and for minimal loss of fluoride.

Purification of the activated carbon by digestion with sodium hydroxide and hydrochloric acid was essential for high recoveries of fluoride, presumably because of the silica and alumina content of the carbon. No search was made for a purification procedure more consistent with retaining the activity of the carbon.

It was of interest to know the volume of water wash required by the anion column after passage of the sample. The data in Table II indicate that excess wash water is not required beyond that necessary to wash all of the sample into contact with the resin. On the other hand, prolonged washing is not detrimental.

The color of the resin changes to a lighter hue when the hydroxide ion is replaced by the anions of the sample. This color change serves to define the volume of the anionic resin occupied by the adsorbed sample and may be augmented, if desired, by staining the resin with an acid-base indicator such as Thymol Blue or Tropaeolin O.

TABLE I

Effect of Pretreatment on Suppression of Interferences and Recovery of Fluoride
(50 ml of preserved urine diluted to 250 ml and passed through column. First 50 ml discarded; remaining 200 ml collected.)

Pretreatment column	Sample	Apparent micrograms F in fractions 1 to 5 from anionic column (7 ml Dowex-1)					Apparent recovery of added F, %
		1	2[1]	3	4	5	
None	Normal	0.0	13.0	19.6	17.5	13.6	78.0
	Spiked	0.0	32.5	19.0	17.5	12.0	
11 ml Dowex 50	Normal	0.0	13.5	18.7	16.6	12.1	70.8
	Spiked	0.2	31.2	17.4	16.0	12.0	
11 ml Charcoal	Normal	0.0	4.3	0.0	0.9	0.2	88.8
	Spiked	0.0	26.5	0.5	0.2	0.0	
11 ml Dowex 50 and 11 ml Charcoal mixed	Normal	0.2	4.2	0.2	0.0	0.0	86.0
	Spiked	0.0	25.7	0.0	−0.2	−0.2	
11 ml Charcoal on top and 11 ml Dowex 50 on bottom	Normal	−0.2	2.5	0.0	0.2	0.0	77.2
	Spiked	−0.2	21.8	0.0	0.0	0.0	
11 ml Dowex 50 on top and 11 ml Charcoal on bottom	Normal	0.0	2.9	0.0	0.0	0.0	94.4
	Spiked	0.0	26.5	0.2	0.2	−0.2	

[1] Fluoride appears in fraction #2. Spiked samples contained 25 micrograms of added fluoride.

To stain the resin, add a few drops of sodium hydroxide solution to a slurry of the purified resin (in the chloride form) and then add a dilute solution of the indicator dropwise until the desired depth of color is obtained.

More than adequate separation of fluoride from phosphate is achieved when no more than 15% of the exchange capacity of a 10-ml volume of anionic resin is occupied by the sample. Under these conditions the fluoride appears in fractions 3 and 4 while the phosphate does not appear at least until fraction 20. Caution must be exercised when interpreting the volume of remaining resin available for chromatographic separation after adsorption of the sample. If as much as 35% of the resin capacity is initially occupied by the sample, the capacity of the column for chromatographic separation of fluoride is nil because of the rapid expansion of the bands to fill the entire column when the eluting solution is added and new equilibrium conditions are established. Because no unoccupied resin then remains, the fluoride and phosphate are eluted simultaneously. The separation of fluoride and phosphate is a function of the volume of resin remaining after allowance has been made for a threefold expansion of the sample bands. This expansion is not observable because the color change is blanked out by the overwhelming effect of the eluting solution on the pH.

The requirement that the sample stand in contact with the anionic resin overnight arises from observations that fluoride and small amounts of interfering substances are eluted contiguously if immediate elution is attempted. On long standing in contact with the anionic resin, the interfering substances are altered and no longer appear in the fractions containing the fluoride.

TABLE II

Effect of Water Wash on Recovery of Fluoride from Anion Column

Volume of wash water, ml	15	65	115	165
Normal urine, mg F/liter found	0.22	0.25	0.25	0.25
Spiked urine, mg F/liter found	2.60	2.60	2.58	2.60
Recovery of added F, %	95.2	94.0	93.2	94.0

Results

While recoveries of fluoride during the developmental work were consistently in excess of 90% and most often near 94%, no assurance could be given that metabolized fluoride in urine specimens would behave in the ion exchange process in like manner to the ionic fluoride added to the test samples. To this end, eight volunteers were given 500-ml portions of water containing 8 mg of fluoride as sodium fluoride with instructions to consume the water within an eight-hour period and to collect either a 12- or 24-hour cumulative urine specimen.

The fluoride in these, as well as in control specimens obtained from each volunteer before ingestion of the fluoride, was separated by both the ion exchange method and a Willard and Winter distillation. The distillation modification followed was that of Smith and Gardner.[15] Final determinations of the fluoride in the distillates were according to the Megregian method while

TABLE III

Comparison of Ion Exchange with Distillation Separation of Urinary Fluoride (Procedure I).

Subject	Fluoride Found, mg/liter			
	Before ingestion		After ingestion	
	Distillation	Ion exchange	Distillation	Ion exchange
A	0.17	0.15	1.49	1.92
B	0.49	0.50	4.06	4.02
C	0.24	0.15	2.12	1.96
D	0.17	0.31	2.64	2.54
E	0.59	0.70	2.49	2.48
F	0.39	0.40	1.89	1.94
G	0.42	0.46	2.38	2.42
H	0.59	0.76	2.82	2.88
Mean	0.38	0.43	2.49	2.52

the modification of this method described herein was used for the ion exchange effluents.

Comparisons of the results obtained by ion exchange with those obtained by distillation are shown in Table III. The close agreement shows that metabolized, excreted fluoride is adequately recoverable by the ion exchange procedure.

The preserving qualities of cationic resin were affirmed in field trials in so far that mold growth was inhibited until the bottles were uncapped for analysis. Thereafter, molds appeared in some of the samples.

Separation Procedure II

ELUTION OF FLUORIDE FROM ACETATE RESIN WITH BERYLLIUM ION

Preservation of samples

Urine specimens should be collected in, or aliquots immediately transferred to, polyethylene bottles containing either a 5-ml volume of dry, 20 to 50 mesh Dowex 50W or 0.2 gram of disodium EDTA for each 100 ml of urine.

Separation of fluoride

Prepare the separation column by adding a few milliliters of water to the chromatographic tube and then a 20-ml volume of a 1:1 slurry of 100 to 200 mesh Dowex 1. When the resin has settled but before the water has completely drained, twirl the tube to level the surface of the resin bed and to dislodge any resin particles adhering to the glass surfaces. Also, before the water has completely drained, add dry sand to a 2-cm depth.

Convert the resin to the acetate form by passing not less than 150 ml of 1*M* sodium acetate through the column and wash the resin bed with several portions of water totaling not less than 50 ml, allowing the water to drain to the sand surface after each addition.

Dilute 10 ml of the preserved urine to approximately 50 ml and pass through the column. One-half of the adsorptive capacity of the resin, as evidenced by the position of the lowest diffuse yellow or brown band, may be used safely. Rinse the reservoir and resin bed with several 10-ml portions of water and then pass 100 ml of 0.1*M* acetic acid through the resin bed.

Elute the fluoride with precisely measured, 25-ml volumes of the Beryllium Eluting Reagent. Collect four fractions and determine the fluoride in each separately. The peak fluoride values are found in the first or second fraction. In summing the fluoride values of the fractions, ignore those fractions in which the value has dropped to a constant level.

Experimental

Preliminary experimentation revealed that: (1) beryllium does not interfere with colorimetric fluoride determinations by highly-acidic, zirconium-lake methods, (2) solutions of beryllium salts rapidly and completely release adsorbed fluoride from anionic resins, and (3) neither fluoride nor those components of urine which interfere with the colorimetric determination of fluoride are released to an appreciable extent from anionic resins by dilute acetic acid. To achieve separation of fluoride from urine, it remained only to establish the optimal combination of beryllium and acetic acid for use as an eluting reagent.

Results obtained by varying the concentration of acetic acid and of beryllium ion while holding the other constant, as presented in Figure 2, show that the rapidity of elution of the fluoride ion increases with higher concentrations of either component. On the other hand, interfering substances in the urine were found to appear in progressively earlier fractions when the concentrations of acetic acid and of beryllium were increased. The composition of the reagent specified for the procedure represents a compromise between these two opposing effects.

Inasmuch as phosphate complexes with beryllium and the phosphate band appears above the fluoride band in the resin column, some adverse effect was to be expected. Figure 3 illustrates the elution of fluoride from columns when fluoride alone is present and when 25 mg of phosphate is present. Included also are the two extremes in rapidity of fluoride elution which were obtained in the analysis of urine specimens by this

procedure. It may be seen that fluoride alone is eluted rapidly even in amounts as great as 500 micrograms, but that phosphate causes a delay in the elution of fluoride by consuming the greater part of the beryllium in the early fractions. In the most favorable urine analysis (presumably dilute or low in phosphate) the fluoride is only slightly delayed while at the other extreme the elution curve is considerably broadened. The broadening should be interpreted not only in light of the delaying action of phosphate but also on the premise that the urine contains other complexing compounds besides phosphate and that less unoccupied resin was available for the chromatographic process because of the concentration of solids in the urine.

When EDTA is used as a urine preservative, a yellow color is eluted from the anionic exchange column by the Beryllium Eluting Reagent unless the column is first flushed with acetic acid. Twenty-five milliliters of 0.1*M* acetic acid were found sufficient to remove the color with most specimens but 100 ml were required for the entire range of urine concentrations encountered. As shown in Table IV the use of the larger volume of acetic acid results in a small loss of fluoride but has justification in the proportionally greater reduction in background interference.

When cationic resin was used as sample preservative, a 25-ml wash with 0.1*M* acetic acid proved sufficient. With either preservative a low level of background interference, proportional to sample size and total solids content, is present. The background also increases if the elution is interrupted for an appreciable interval between fractions. The error due to this background interference may be minimized by ignoring the apparent fluoride values obtained in fractions subsequent to the one in which the fluoride value has dropped nearly to the background level. The extent to which this background level contributes to the fluoride values found in the first two fractions could not be determined because of inadequate precision and accuracy of both the distillation and ion-exchange methods at normal levels of fluoride excretion.

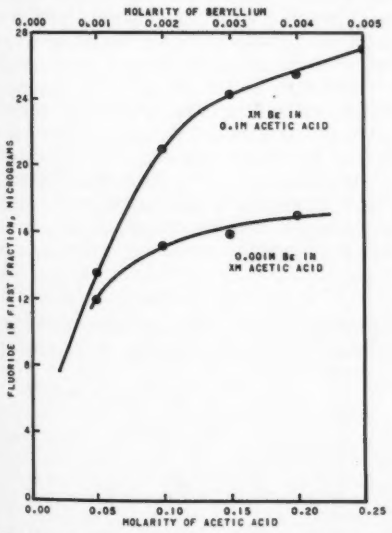

FIGURE 2. Effect of beryllium and acetic acid concentrations on rapidity of fluoride elution. (Serious interference appears in the 5th 25-ml fraction with 0.01M Be, and in the 7th 25-ml fraction with 0.2M acetic acid.

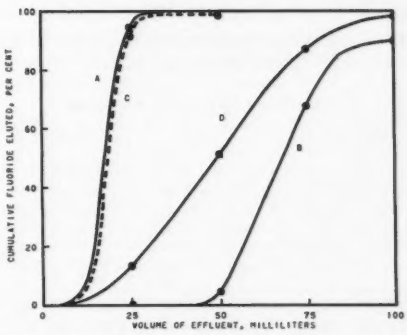

FIGURE 3. Delaying effect of phosphate on elution of fluoride.

A. 500 micrograms fluoride in water.

B. 30 micrograms fluoride and 25 milligrams of phosphorus as phosphate in water.

C and D. Extremes of urine specimens analyzed.

TABLE IV

Effect of Volume of Acetic Acid Wash on Recovery of Fluoride and Reduction of Interferences

Urine aliquot, ml	Added F, micrograms	0.1*M* Acetic acid wash, ml	Apparent F in 25-ml fractions, micrograms				Recovery of added F, %
			1	2	3	Total[1]	
10	Normal	25	5.5	1.4	1.4	8.3	99.2
10	25.0	25	28.9	2.5	1.7	33.1	
10	Normal	100	3.8	1.3	1.2	6.3	97.6
10	25.0	100	27.4	2.3	1.0	30.7	
25	Normal	25	12.9	4.1	3.9	20.9	99.5
25	62.5	25	72.0	7.4	3.7	83.1	
25	Normal	100	8.8	3.5	2.5	14.8	98.1
25	62.5	100	64.8	8.4	2.9	76.1	

[1] Ordinarily the apparent fluoride in fraction 3 would be ignored.

TABLE V

Effect of Fluoride Concentration on the Elution with Beryllium Ion

F added to urine, micrograms	F found in 25-ml fractions, micrograms				Recovery, %
	1	2	3	4	
None	2.5	1.6	0.7	0.0	—
25	14.7	11.0	2.3	0.5	94.8
50	26.4	22.0	4.0	0.5	96.2
100	47.7	45.0	10.0	1.6	99.5
200	70.5	102.6	27.8	2.8	99.4

[10 ml Dowex 50 preserved urine diluted to 50 ml and adsorbed on Dowex 1 (OH). Dowex 1 then converted to acetate with 150 ml of 0.1*M* acetic acid and fluoride eluted with 0.001*M* Be in 0.1*M* acetic acid.]

TABLE VI

Precision of Analysis

Preservative	F added, micrograms	No. of analyses	Mean apparent F in fractions 1 to 3, micrograms			F found,[a] micrograms	Standard deviation	Mean recovery %
			1	2	3			
None	None	6	4.5	1.2	1.0	3.7	0.2	93
	25	6	26.9	2.2	1.1	26.9	0.2	
EDTA	None	6	3.9	1.0	0.9	3.1	0.3	97
	25	6	27.4	1.8	0.9	27.4	0.2	
Dowex 50	None	6	3.0	1.2	0.6	3.0	0.5	100
	25	6	27.3	2.0	0.6	28.1	0.3	

[a] Sum of apparent F in fractions 1 and 2 minus twice the apparent F in fraction 3.

Repeated blank determinations have shown the fluoride contribution by reagents to be less than one microgram per determination.

The data of Table V were obtained to evaluate the adequacy of the method for the separation of fluoride in the concentration range to be expected in industrial exposures. In this experiment, urine preserved with Dowex 50 was adsorbed on the hydroxide form of Dowex 1 resin. The resin was then converted to acetate with an excess of 0.1*M* acetic acid and the fluoride eluted with 0.001*M* beryllium in 0.1*M* acetic acid. This variation of the procedure is also an acceptable one particularly for samples preserved with cationic resin. The results obtained with it indicate that the fivefold increase in beryllium ion later adopted is sufficient to assure complete elution of the fluoride in the first four fractions. The progressively higher recoveries with increasing fluoride content of the sample point to a constant loss of about one microgram.

The precision of the ion exchange method was obtained using a pooled urine specimen, half of which was spiked with 2.5 micrograms of fluoride per milliliter. Ten-ml aliquots of the normal and spiked urine were analyzed in the fresh state and also after the addition of EDTA and Dowex 50. A summary of these analyses is given in Table VI. The percentage recovery figures for added fluoride are approximate inasmuch as the true value of the normal fluoride content of the urine was not known. The distillation method has not been sufficiently precise in our hands to warrant an assumption that analyses obtained with it represent the true concentrations of fluoride in normal urine.

Results

Duplicate aliquots of the urine specimens which represented excretion of ingested fluoride and which were used to obtain the data of Table III had been preserved with EDTA. Six of these specimens remained free of sediment and mold growth at the end of six months and were analyzed by the described procedure. The results are compared in Table VII with the analyses previously obtained with a Willard and Winter distillation.

Comparative results were also obtained on a series of 53 specimens from men having industrial exposures to fluoride among whom the individual, unintegrated, fluoride excretion levels ranged from 1.5 to 14 mg per liter. Willard and Winter distillations were performed on aliquots preserved with alcoholic thymol while aliquots preserved with Dowex 50 were used for the ion exchange separations. The mean obtained by the Willard and Winter distillation was 5.55 mg per liter and by the ion exchange method, 5.84 mg per liter. The mean of the percentage differences between the results by the two methods was 8.2.

In a second series of 10 specimens obtained from men in another industry, covering uninte-

TABLE VII

Comparison of Ion Exchange with Distillation Separation of Urinary Fluoride (Procedure II).

Subject	Fluoride Found, mg/liter	
	Distillation	Ion exchange
A	0.17	0.19
B	4.06	4.52
C	2.12	2.03
E	2.49	2.53
F	0.39	0.30
G	2.38	2.72
Mean	1.94	2.02

grated excretion levels from 1 to 16 mg per liter, a mean value of 5.60 mg per liter was obtained by the distillation method and 6.26 by the ion exchange method. The ion exchange results were 6.7 per cent higher on the basis of the mean percentage difference. In this series the specimens were preserved with Dowex 50 for both the distillation and ion exchange analyses.

The consistently higher results obtained by the ion exchange method indicate that the efficiency of fluoride separation is greater than that of the distillation method. In a test of the distillation method with eight urine samples containing 2.5 mg per liter of added fluoride, recoveries ranged from 65 to 98 per cent with a mean of 87 per cent.

Conclusions

The ion exchange procedures described provide simple, low-cost alternatives to the distillation process for the separation of fluoride from urine. While ion exchange methods are not rapid in the sense of obtaining individual results quickly, the simplicity of the apparatus and the fact that the operations proceed without constant attention allow the simultaneous processing of a large number of samples and the attainment of an over-all rapidity of analysis.

The first procedure described is somewhat critical with respect to maximal volume of the urine aliquot subjected to analysis but, aside from this limitation, is capable of providing results equivalent to those obtained by distillation procedures.

The second procedure has a low level of background interference which restricts the accuracy obtainable at normal excretion levels. Inasmuch as the intent of the work was to provide a means for evaluating the success of control measures for the protection of the industrial population in which the fluoride excretion level at times exceeds tenfold the normal, it can be stated that the procedure possesses the required validity.

It has been evident throughout this work that the ion exchange process *per se* is accurate and precise and, with due regard to the behavior of interferences in the exchange column, has applicability to the determination of fluoride in a diversity of materials.

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Air Flow Resistance of Flexible Metal Hose

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Introduction

FLEXIBLE hose and ducts constructed from a variety of materials are widely used when sections of an exhaust system must move to follow moving machine parts or shifting operations and when the exhaust ventilation system is of a temporary nature. Flexible metal hose of galvanized or stainless steel construction is especially applicable when handling solvents, corrosive chemicals or pyrophoric metals such as magnesium, uranium and zirconium. Although flexible metal hose has been used for these and other air handling purposes for many years, reliable data on friction losses of straight runs and elbows have not been available from the manufacturer or from other sources. It has been common practice to assume that the air flow resistance of flexible metal hose is either that of an equivalent size of standard round galvanized sheet metal duct or that it is the same as that of spiral, wire-bound flexible cloth hose.

The objective of the present investigation was to determine accurate friction values for the several sizes of flexible metal hose commonly used for exhaust ventilation service in machine shops and similar installations. In addition, a correlation between the resistances of equal sizes of corrugated and standard sheet metal duct was sought so that friction charts and tables pertaining to standard sheet metal duct could be used, with suitable correction factors, for estimating the resistance of corrugated metal duct.

Test Method

Air flow resistance measurements of 4, 5, and 6 inches I.D. "Lightweight U.I. Flexible Steel Hose" manufactured by the Metal Hose Division of The American Brass Co. (Figure 1) were made at duct velocities from 1000 to 5000 fpm for straight runs and for 90° and 180° elbows of various radius ratios.

The arrangement of apparatus for making the air flow resistance measurements is illustrated in Figure 2 which shows: (1) flow-straightening inlet section, (2) calibrated orifice-type flow meter, (3) inclined (1/10) and vertical U-Tube alcohol-filled manometers for measuring differential pressure across flow meter, (4) up-stream static pressure tap, (5) elbow formed with the aid of curves chalked on the ground, (6) down-stream static pressure tap, (7) alcohol-filled inclined (1/10) and vertical U-Tube manometers for measuring differential pressures (pipe resistance), (8) slide damper to regulate air flow, and (9) motor and centrifugal exhauster.

The air flow resistance characteristics of 20-foot long sections (expanded length) of straight flexible hose were measured when fully expanded, or stretched. Similar measurements were made when the corrugations were squeezed together so as to compress the hose to its minimal length. For the 4- and 6-inch diameter hoses, the measured difference between expanded and compressed length was 38 inches per 20 foot piece while for the 5-inch diameter hose, it was 51 inches. (The hose is sold on the basis of the expanded length and in actual use it tends to assume a length between the two extremes.)

When fully compressed, the spirally-wound interlocking metal strips making up the hose wall lie close together and produce an unexpectedly smooth and uniform wall surface. When fully expanded, the layers of the inner metal spiral separate slightly and produce alternating lands and grooves approximately 3/16 inches wide and 1/16 inches deep.

Bends are made by compressing the spiral windings along the inside radius of the bend and expanding them on the outer radius. Each diameter of hose has a minimum bending radius related to the separation of adjacent spiral windings. It appears to be possible to produce a greater degree of duct compression with the smaller duct diameters; as evidenced by an ability to form elbows of smaller radius ratios. These minimum radii are noted in Table I which lists all the straight lengths, angles and elbow radius-ratios tested.

Results

Figure 3 shows graphically the air flow resistance of straight lengths of corrugated metal hose

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of various diameters. Resistance per hundred linear feet is given for each hose when fully expanded and when fully compressed. (In this case, hose length refers to the actual measured length for each condition.) Intermediate values, obtained by interpolation between the two curves, represent average values useful for most practical applications.

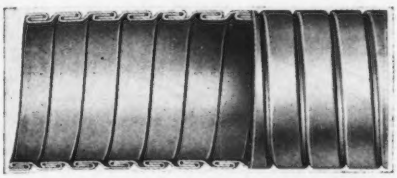

FIGURE 1. Flexible metal hose construction.

For each hose diameter tested, air flow resistance per hundred linear feet of fully-expanded hose was greater (16% greater for 4- and 6-inch hose and 29% greater for 5-inch hose) than the resistance of an equal length of compressed hose. This reflects the greater surface roughness of the interior of the expanded hose, which was noted previously.

In Table II, the air flow resistance of 4- and 6-inch diameter flexible metal hose has been

FIGURE 2. Arrangement of apparatus for air flow resistance measurements.

TABLE I

Catalogue of Air Flow Resistance Measurements

Hose diam. inches	Hose Length		Duct Velocity Range		Radius Ratios of Measured 90° Elbows[2]			Radius Ratios of Measured 180° Elbows[2]		
	expanded	compressed	min. (fpm)	max. (fpm)	min.[1]			min.[1]		
4	20 ft 1 in.	16 ft 11 in.	975	5080	2.5	6.0	10.0	4	6	10
5	20 ft 0 in.	15 ft 9 in.	845	4180	3.5	6.0	10.0	—	—	—
6	19 ft 10 in.	16 ft 9 in.	740	2990	4.5	8.0	12.0	—	—	—

[1] Minimum radius ratio.

[2] Center line radius of curve/hose diameter.

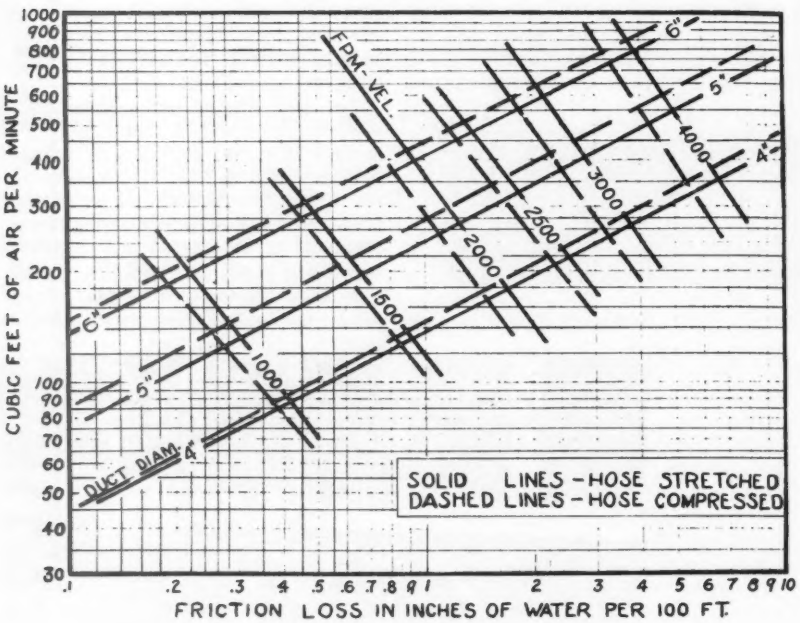
CUBIC FEET OF AIR PER MINUTE
FRICTION LOSS IN INCHES OF WATER PER 100 FT.
FPM-VEL.
DUCT DIAM.
SOLID LINES - HOSE STRETCHED
DASHED LINES - HOSE COMPRESSED

FIGURE 3. Duct friction chart.

TABLE II

A Comparison of Friction in Straight Ducts of Different Construction

Duct Construction	Friction per 100 ft of straight hose—inches of water gage							
	1000 fpm vel.		2000 fpm vel.		3000 fpm vel.		4000 fpm vel.	
	4" diam.	6" diam.	4" diam.	6" diam.	4" diam.	6" diam.	4" diam.	6" diam.
lt.wt. collapsible spiral wire reinforced fabric hose*	.95	.66	3.6	2.5	7.8	5.4	15	9.4
close-pitched spiral wire reinforced fabric hose*	1.0	.74	3.8	2.9	9.2	6.3	16	12
galvanized sheet metal round duct**	.50	.30	1.9	1.1	4.0	2.4	7.0	4.2
U.I. lt.wt. flexible metal hose—(extended length)	.41	.22	1.7	.92	3.7	2.1	6.5	3.8

* Resistance values from Bulletin #44, The Flexaust Co., N. Y., 17.

** Resistance values from Heating, Ventilating and Air Conditioning Guide, ASHACE, New York 13, N. Y.

compared at selected duct velocities with the resistance of two types of commonly-used non-metallic flexible hose and with standard sheet metal duct. It may be noted that the friction of the fully-stretched 6-inch diameter U.I. Lightweight Flexible Metal Hose is, on the average, only 85% of the resistance of 6-inch standard sheet metal duct; and that the resistance of 4-inch diameter flexible metal hose is only 90% of 4-inch round sheet metal duct. Since friction loss is lower when flexible metal hose is fully compressed, the reduction, when compared to standard sheet metal duct, is even more marked than the values cited above. In contrast, the flexible wire-wound fabric ducts have air flow resistances approximately double those of standard sheet metal duct of equal diameter.

Air flow resistance of elbows is shown in Table III. Ninety degree elbows of U.I. Lightweight Flexible Metal Hose were tested at three curvatures, expressed as the ratio of centerline duct radius to duct diameter. In addition, the

TABLE III

Elbow-Losses

Duct diam. inches	Elbow radius ratio	Elbow Resistance			
		No. of duct diameters of straight hose having equal resistance		Fractional velocity head loss	
		90° elbows	180° elbows	90° elbows	180° elbows
4	2.5*	0	—	0	—
4	4.0	—	6.0	—	.11
4	6.0	0	5.0	0	.09
4	10.0	1.5	6.0	.044	.11
5	3.5*	2.5	—	.052	—
5	6.0	3.5	—	.075	—
5	10.0	2.5	—	.054	—
6	4.5*	7.0	—	.12	—
6	8.0	5.0	—	.09	—
6	12.0	7.0	—	.12	—

* Minimum elbow radius ratio.

air flow resistance of 180° elbows was measured with the 4-inch diameter hose.

For many measurements, the air flow resistance of a 20-foot length of hose was less with a 90° elbow in it than when the entire hose was stretched out straight. This was especially true for the 4-inch diameter hose. An explanation is that there is an actual shortening of the overall duct length due to partial compression at the bend and this, in turn, produces a smoother duct surface at the inside radius of the bend. In short, the reductions in friction due to (1) an actual shortening of the hose and (2) a decrease in duct roughness due to the contraction were greater than the added resistance of the bend. It should be noted, however, that the differences were very small and may not have been within the range of assured accuracy of the measurements.

The resistance of four-piece 90° galvanized elbows is given in the ASHACE Guide as equivalent to 10 diameters of straight pipe for radius ratios of 3 to 12 and double this value (*i.e.* 20 duct diameters) for 180° bends. It may be seen from Table III that the resistances of the flexible metal hose elbows that were measured were less than for the same size of sheet metal elbow. In explanation, it should be noted that sheet metal elbows are constructed from short straight sections of duct and therefore they are not smooth curves but, rather, a series of chords of a curve.

Summary

Measurements of straight runs and elbows of clean 4-, 5- and 6-inch round flexible metal hose indicate that friction losses are somewhat less than for standard round galvanized sheet metal ducts and less than one half those of equal sizes of commonly-used fabric-type flexible hoses. Figure 3 gives values for estimating friction loss of straight runs and Table III shows appropriate values for estimating elbow losses. Standard sheet metal friction charts such as those published in the ASHACE Guide may be used for estimating resistance of flexible metal hose without serious error; differences will be on the conservative side.

Acknowledgments

The authors wish to acknowledge the valued assistance and support of Nuclear Metals, Inc., Concord, Massachusetts in the conduct of this investigation. The Metal Hose Division of the American Brass Co. kindly lent their products for measurement.

AIR POLLUTION MANUAL

THE AIR POLLUTION TECHNICAL COMMITTEE of the American Industrial Hygiene Association has completed a valuable new publication, *Air Pollution Manual: Part I—Evaluation*. The various chapters of the manual have been compiled and written by men outstanding in their fields. The contents include: Legislation and Administration, Community Relations, Concentrations of Pollutants, Biological Effects, Effects on Vegetation, Effects on Farm Animals, Economic Factors, Sampling, Chemical Procedures, Odors, Radioactive Substances, and Meteorology. This volume will become a necessity on the desk of industrial hygienists, air pollution control engineers, plant engineers, plant managers, public health and municipal authorities, and many others. Already a reconstituted committee is beginning the preparation of *Part II—Control*.

Orders for *Part I—Evaluation* should be sent to George D. Clayton, Executive Secretary, American Industrial Hygiene Association, 14125 Prevost, Detroit 27, Michigan. The price is $5.50 per copy to AIHA members and $8.50 to non-members.

A Mass Loading and Radioactivity Analyzer for Atmospheric Particulates

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THE mass concentration of particulate in the atmosphere is usually measured by weighing samples collected on filters by high volume samplers in a 24 hour period.[1] Because of the necessity of separately weighing each filter before and after sampling, this technique does not allow automation of sampling, simple measurement, and data printout in the manner which has already been achieved in optical measurements (transmittance and reflectance) of particulate collected on tape filters.[2, 5] It has been repeatedly shown, however, that optical measurements do not universally correlate with mass concentration. Some correlation between optical and weight values has been established for some particulate pollution of a specific community on the basis of empirical calibration.[3, 6] Even in such an instance, color differences between winter and summer samples require separate calibrations. Furthermore, correlation developed for a coal burning city is not applicable to a city which has, for example, high dust concentration as a result of dust storms.

Therefore, despite the availability and utility of some excellent soiling index instrumentation, there remains a real need for an analytical technique which gives values that: (1) directly correlate with mass; (2) are unaffected by color; (3) allow data from various cities and in different seasons to be merged for analysis; and perhaps most important of all, (4) allow short term (2 to 8 hour intervals) concentration measurements of atmospheric particulate to be reported in the same units ($\mu g/m^3$) as weighed long-term (24-hour interval) samples. This use of shorter averaging periods will result in concentration values more indicative of peak concentrations (albeit not instantaneous peaks) recommended by the National Conference on Air Pollution.[11] Where both 24-hour and shorter period sampling are carried out, the accuracy of these measurements can be checked since the sum of short term measurements should equal the equivalent long term measurement. Furthermore, short term concentration measurements can themselves serve as indices of particulate pollution and can show variations introduced by related meteorological conditions such as temperature inversions and air mass movements.

It was with the need of the above type of measurement system in mind that the previously reported[9] SEC high flowrate membrane tape sampler was developed. (Millipore microweb tape, type WS, consists of a nylon screen impregnated with a cellulose acetate ester. Manufactured by Millipore Filter Corporation, 36 Pleasant Street, Watertown 72, Massachusetts.) The above paper reports the adaptability of particulate samples collected by the tape sampler to a beta gauging technique[13, 14] which meets the desired objectives. In the application of this technique, the storage cartridge, containing the spots of particulate deposit (2 cm^2 areas on the membrane surface), is attached to the mass loading analyzer described herein. In this instrument, the tape is placed between a beta radiation source and a beta radiation detector, an arrangement referred to as "geometry" in which a fraction of the source radiation reaches the detector after passing through the tape and particulate deposit. The greater the mass of the particulate spot, the less is the amount of radiation reaching the detector and being counted. By correcting for the mass of the tape medium, the radioactivity in the sample deposit, and natural background radioactivity, the net effect due to the mass of the particulate on the tape is obtained. This beta gauge method of mass loading analysis is applicable to various filter media including paper and fiber glass materials. The membrane filter offers the advantage of collecting the particulate on its surface with a minimum of penetration into the tape. This type of collection lends itself more favorably to other additional analyses such as radioactivity, particle counting, and particle sizing.

This method of analysis offers the advantages of nondestructive physical measurement and rapid, automatic operation which is desirable in handling large amounts of data. It is further

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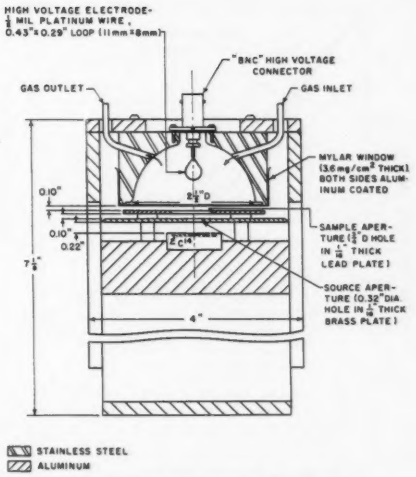
adaptable to the use of a central beta gauge unit to readout the loadings of a number of filter tapes from sampler locations at a number of points in a city, state, or nation. The detector and associated electronics of the beta gauge readily permit analysis of atmospheric particulate for both natural and artificial radioactivity. The measurement of mass, optical transmission or reflectance, and radioactivity on the same spot can yield data which may be quite informative as to the character of the particulate on the tape and the environment from which it was collected.

Beta Gauging Measurements

In the beta gauge method, the energy of the source radiation determines the degree to which a given mass of absorber will reduce the radiation. Low energy radiation is more readily absorbed than high energy radiation. Therefore, a sensitive method for measurement of small amounts of matter requires a low energy radiation source, *i.e.*, an absorption curve with a steep slope showing large changes in absorption for small changes in mass. Likewise, greater density materials call for higher energy radiation.

A study was made of absorption curves of different energy beta emitters having long half-lives (carbon-14: 0.155 mev, 5568 yr.; cesium-137: 0.523 mev, 33 yr.; and thallium-204: 0.765 mev, 3.5 yr.). Carbon-14 had the steepest absorption curve and at the same time sufficient energy to keep the radiation from being totally absorbed by the membrane tape. A source of carbon-14 (3 millicuries) was obtained with the activity deposited over a 13/16 inch diameter area of a ¼ inch thick brass planchet (Tracerlab, Inc.). It is covered by a thin plastic film to keep it intact and sealed to prevent dispersal of the active material and contamination of the environment. The source has the maximum specific activity available to give optimum counting statistics for short counting intervals. Furthermore, it provides an activity sufficiently high that background activity is relatively insignificant.

A gas flow end-window proportional counter is used as a detector for beta and alpha radiation (Figure 1). The detector was developed to give maximum counting efficiency without going to an internal counter which would be impractical for this purpose. It was constructed using the 2½ inch diameter hemispherical dome taken from an internal counter (Nuclear Measurements Corp.). The end window was made by covering the base with thin (3.6 mg/cm²) mylar film coated on both sides with aluminum to reduce build-up of static charge. A 0.0005 inch diameter platinum wire was used for the high voltage electrode. It was loop shaped and positioned to give a good count vs. voltage plateau.[10] Operating voltage in the beta proportional region was taken at 1600 volts which lies within the plateau of the curve. A similar voltage plateau exists for alpha counting and the operating voltage in this case was 925 volts.



DETECTOR AND SOURCE ASSEMBLY FOR MASS LOADING ANALYZER

FIGURE 1.

In addition to the nature of the radiation and the absorbing medium, the relative physical arrangement of source, absorber, and counter has an important effect on the slope of the absorption curve. Several arrangements were investigated using various thicknesses of aluminum to simulate particulate mass on the filter (Figure 2): the absorber was placed closer to the detector and the source more distant (Curve I); in the reverse situation the absorber was closer to the source (Curve II); and the source was masked to effectively make it a point source relative to the absorber and detector window diameters (Curve III). The best absorption curve (III) was obtained when the source diameter was reduced to a 0.23 inch diameter area. However, this resulted in a significant and undesirable reduction of counting activity. The final arrangement (Curve IV) was selected as a compromise in which a high level of activity was maintained and the absorption curve was not very significantly different from the optimum. In this arrangement (Figure 1) a brass masking plate of sufficient thickness (1/16 inch) is placed

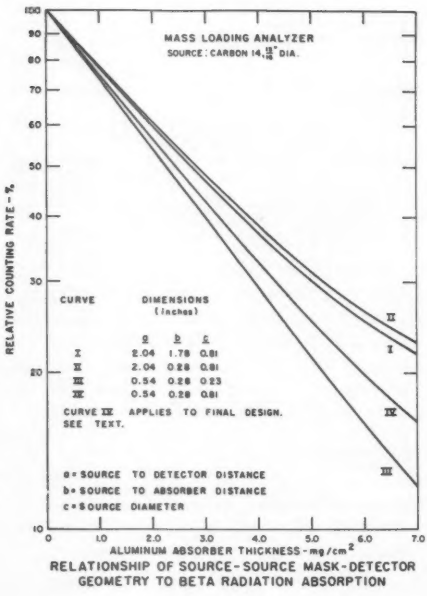

MASS LOADING ANALYZER
SOURCE: CARBON 14, 13/16" DIA.
RELATIVE COUNTING RATE - %
CURVE
DIMENSIONS (inches)
a b c
I 2.04 1.78 0.81
II 2.04 0.28 0.81
III 0.54 0.28 0.23
IV 0.54 0.28 0.81
CURVE IV APPLIES TO FINAL DESIGN. SEE TEXT.
a = SOURCE TO DETECTOR DISTANCE
b = SOURCE TO ABSORBER DISTANCE
c = SOURCE DIAMETER
ALUMINUM ABSORBER THICKNESS - mg/cm²
RELATIONSHIP OF SOURCE-SOURCE MASK-DETECTOR GEOMETRY TO BETA RADIATION ABSORPTION

FIGURE 2.

between the source and the tape to totally absorb any unwanted radiation. It has a 9 mm diameter aperture to restrict the radiation to a circular beam which then passes through the center of the spot deposit.

The prototype instrument was designed to automatically handle the membrane tape from the spiral cartridge in which it is stored after sampling. An additional empty cartridge is used to store the tape after it is analyzed by the beta gauge detector. Two indexing switches, utilizing the indexing holes of the tape, are programmed to alternately position blank and spot portions of the tape under the detector for analysis. Programming is set by an automatic recycling timer which determines the time span of the counting interval according to a specified preset value ranging from 15 seconds to 15 minutes. One of the indexing switches can be readily disengaged to permit either blanks or spots to be analyzed consecutively.

A laboratory type scaler provided the high voltage for the detector and counted the detected radiation. This manual form of operation was used in evaluating the performance of the detector and the sensitivity of the method. A transistorized high-voltage supply and count rate circuit have been developed and are presently undergoing performance evaluation for automatic counting and data recording. Plans are to record the result of each spot analysis directly in terms of mass concentration, *i.e.*, micrograms per cubic meter. This would depend upon empirical calibration data based on a knowledge of a set of constant values for the sampled air volume and the analyzed spot area.

Radioactivity Measurements

Measurement of either alpha or beta radioactivity is made by operating the proportional counter at the corresponding alpha or beta voltage plateau in the proportional region. These measurements are made by totally shielding the carbon-14 source so that the device no longer operates as a beta gauge, thereby making the detector responsive to only the radioactivity of the sample (plus, of course, natural background radiation). A lead shield with a circular aperture is located between the detector window and the tape to restrict the detector's view of the tape to only the one sample spot under analysis for radioactivity. This shield does not affect in any way the operation of the instrument as a mass loading analyzer.

Measurement of artificial radioactivity in atmospheric particulate can be made at any time subsequent to sampling because the half-life of such activity is relatively long (4-6 months). Natural radioactivity, however, has a very short half-life (26.8 minutes for 90% of the activity and 10.6 hours for the remainder) and requires counting immediately after sampling, particularly since in such small samples total activity is quite small.[12]

The possibility of natural or artificial radioactivity occurring in the particulate deposit and acting as an interference in the operation of the mass loading analyzer was anticipated. Under normal circumstances the time between sampling and mass loading analysis is sufficient to have allowed the greater part of the natural radioactivity present to have decayed to an insignificant level. However, consideration must be given to the interference that would occur if samples were read for mass loading immediately after sampling as well as to the longer lived interference from the artificial radioactivity in the sample. This interference is accounted for by first counting the sample deposit for radioactivity and accordingly correcting the subsequent mass loading analysis. In manual operation this correction is done in calculating the net count by treating the natural or artificial radioactivity as background activity and subtracting it from the gross activity. In the design currently being worked on for automatic operation, the results of the radioactive analysis can be temporarily stored, and subsequently, subtracted

electronically from the mass loading analysis to give the corrected answer.

Performance and Discussion

Source activity counted by the detector through the source and detector apertures without any tape or particulate absorption was 2.5×10^5 cpm (counts per minute) $\pm$ 0.3%. (The statistical deviations of count rate in this report are given as percentages of the count rate and these have been calculated at the 95% confidence level unless specified otherwise.) Background counting rate with the source completely shielded was 60 cpm $\pm$ 6½%. This value also applied when the source was withdrawn from the instrument, thereby confirming the effectiveness of the shielding.

Absorption curves (Figures 3 and 4) were determined for aluminum, membrane filter material, and particulate loadings and are specific to the source-absorber-detector geometry of the instrument. The absorber thicknesses, expressed in mg/cm², were calculated from measured areas and weights. The small mass values (approximately 20 mg consisting of 2 cm² particulate deposit on 4.45 cm² membrane filter) required the use of a microbalance (Cahn Electrobalance) which is of sufficient sensitivity to permit readings within $\pm$10 μg. Aluminum absorption data

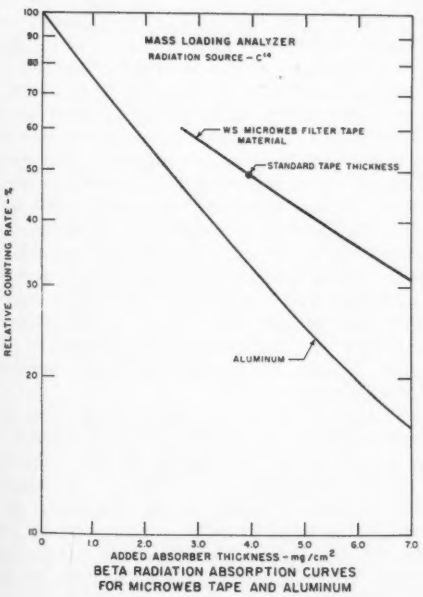

MASS LOADING ANALYZER
RADIATION SOURCE – C¹⁴
WS MICROWEB FILTER TAPE MATERIAL
STANDARD TAPE THICKNESS
ALUMINUM
RELATIVE COUNTING RATE - %
ADDED ABSORBER THICKNESS – mg/cm²
BETA RADIATION ABSORPTION CURVES FOR MICROWEB TAPE AND ALUMINUM

FIGURE 3.

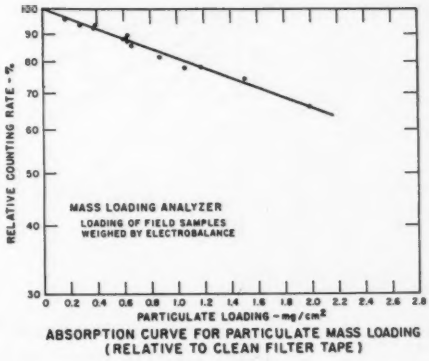

MASS LOADING ANALYZER
LOADING OF FIELD SAMPLES WEIGHED BY ELECTROBALANCE
RELATIVE COUNTING RATE - %
PARTICULATE LOADING – mg/cm²
ABSORPTION CURVE FOR PARTICULATE MASS LOADING (RELATIVE TO CLEAN FILTER TAPE)

FIGURE 4.

confirmed the maximum beta range (29 mg/cm²) for carbon-14 and also showed the production of "Bremsstrahlung" (an electromagnetic radiation resulting from excited nuclear state of electrons bombarded by beta radiation) which decreases the slope of the absorption curve, thereby decreasing the sensitivity. Different thicknesses of membrane tape were investigated and gave an absorption curve significantly different from the curve for aluminum.

A production length of the membrane tape as presently manufactured was examined for uniformity of thickness throughout its length in a 100-foot roll. The results of 32 beta gauge measurements randomly spaced through the roll showed a mean thickness of 3.91 mg/cm² with a standard deviation of $\pm$4.3% of the mean.

Uniformity of the particulate collected on the membrane tape through the area of the deposit was investigated using the beta gauge with a 0.10 inch diameter aperture. Readings of ten corresponding areas were taken along two major diameters (right angles to each other) of the sample spot. Results showed uniform deposition within about $\pm$1% of the mean value.

Various thickness deposits of atmospheric particulate collected on membrane tape under field conditions were used to obtain the absorption curve for dust loadings. This curve (Figure 4) gives the absorption for membrane tape with a spot deposit relative to the clean (blank) tape. Sensitivity of the beta gauge for thickness measurements is determined from this empirical set of values. It is the change in relative count per unit change of loading thickness. There are various sources of error, however, which will give a change in relative count, namely, non-uniformity in tape thickness, variations in sampling flow-rate, statistics of counting, etc. These are presently being evaluated to determine the sensitivity

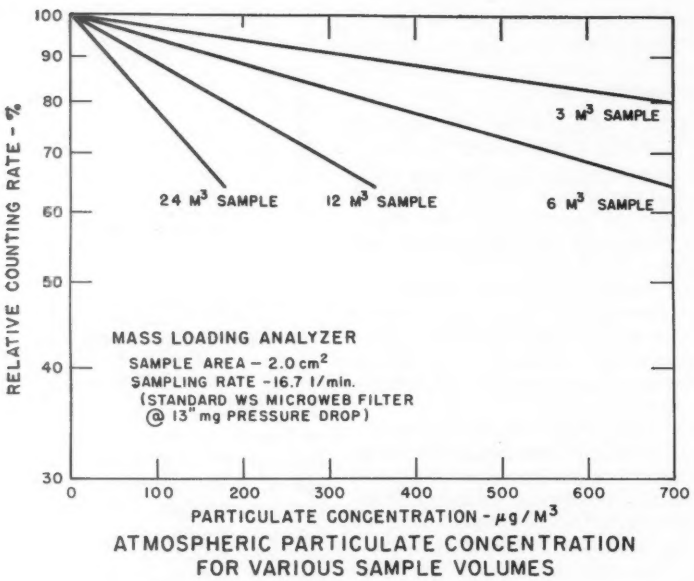


FIGURE 5.

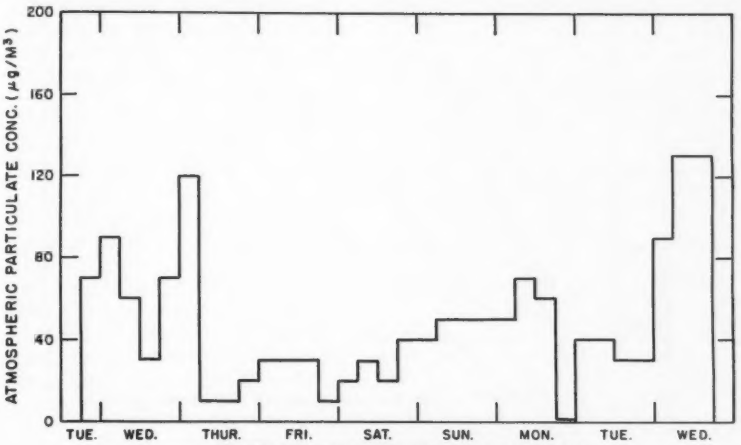
as it is limited by the value of these combined errors.

The significance of the beta gauge technique applied to atmospheric particulate measurements is made more apparent by expressing the deposit thickness directly as atmospheric particulate concentration (Figure 5). Expressed in this manner, the data explicitly shows the sampled volume as a parameter affecting the sensitivity of the method. Thickness measurement sensitivity is improved by sampling larger volumes of air and this will be necessary, especially in atmospheres having low concentrations of particulate.

The choice of sampled volume is dependent on the ultimate objective for which the data is being obtained. If the objective is a study of short term variations, small sampling intervals are required. Sampling interval and air flowrate, limited to the capacity of the sampling instrument, determine the sampled volume. The data of Figure 5 is for a sampler operating near maximum capacity for the standard membrane tape. A family of similar curves is obtained for any flowrate within the range of values to which the sampler can be adjusted. The final choice of sampled volume is a compromise between the desired sensitivity and the minimum sampling interval required.

A mass loading analysis was made of a length of membrane tape on which a series of consecutive six-hour samples of atmospheric particulate was obtained over a period of eight days in an industrial environment. The sampled air flowrate was 16.7 liters per minute, giving a sampled volume of 6 cubic meters. The spot deposits and blank tape between spots were read on the mass loading analyzer. The ratio of the reading for the spot deposit to the average reading of the adjacent blank tape on either side of the sample gave the relative count. Concentration values were obtained using the data of Figure 5. The result (Figure 6) is an example of relatively short term sampling and gives preliminary indications that the method is sensitive to concentration values within 100 $\mu g/m^3$ and shows atmospheric dust loading variations within 24 hour periods. Additional empirical data on the combined errors and their contribution, "noise", in the observed variation will be required to determined the point beyond which concentration variations are significant.

The ability of the counter to detect alpha and beta radioactivity in the particulate deposit is dependent on the detector's efficiency. For the physical arrangement used in this instrument the counting efficiency of the detector is 45% for beta counting of artificial radioactivity. This was experimentally determined by using a National Bureau of Standards calibrated solution of thallium-204 (closely approximating the energy of mixed artificial radioactivity) deposited

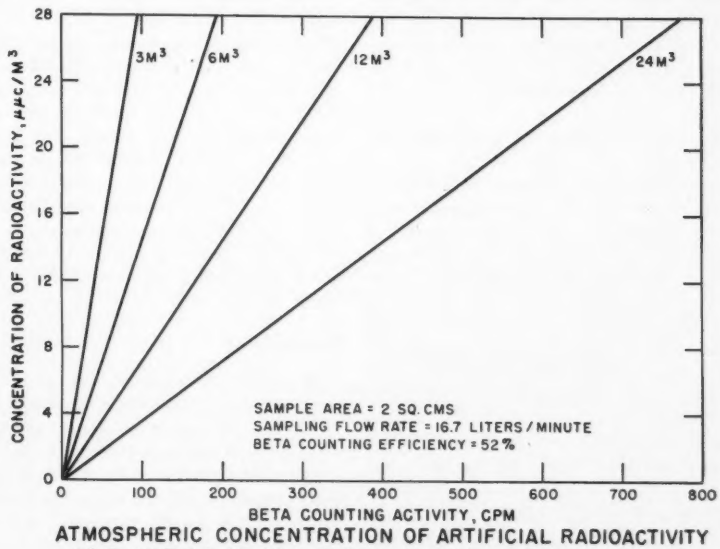


ATMOSPHERIC PARTICULATE CONCENTRATION IN AN INDUSTRIAL AREA
(BY MASS LOADING ANALYSIS)

FIGURE 6.

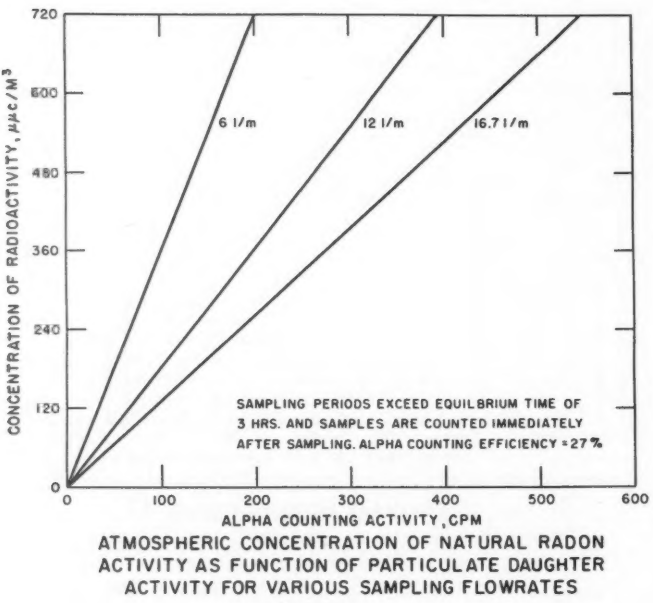
on mylar film to simulate the particulate deposit on the membrane tape. This standard was measured in the same arrangement used for the particulate deposit. In the future revised instrument, a one mg/cm² mylar window will be used for the detector instead of the 3.6 mg/cm² window used in the present prototype. This change should increase the beta counting efficiency of the system to 52%.

A uranium oxide source calibrated in an internal counter was used as a reference standard for determining the alpha counting efficiency of



ATMOSPHERIC CONCENTRATION OF ARTIFICIAL RADIOACTIVITY
AS FUNCTION OF COLLECTED PARTICULATE ACTIVITY FOR
VARIOUS SAMPLED VOLUMES

FIGURE 7.



ATMOSPHERIC CONCENTRATION OF NATURAL RADON ACTIVITY AS FUNCTION OF PARTICULATE DAUGHTER ACTIVITY FOR VARIOUS SAMPLING FLOWRATES

FIGURE 8.

the detector. This efficiency was found to be very low (approximately 2.7%) due to the large window-thickness relative to the range of an alpha particle (3.6 vs 11 mg/cm²). It is anticipated that very thin mylar (approximately one mg/cm²) which will be used to replace the detector window will significantly improve the detection efficiency to approximately 27% for alpha particles.

Calculated activity values for particulate deposits on the basis of a range of atmospheric concentration values for artificial radioactivity give a family of curves with sampled volume as a parameter (Figure 7). A similar family of curves exists for natural radon concentrations with sampling flowrate as a parameter (Figure 8). The range of concentrations was chosen to represent values found in reported studies,[7] and the activities were calculated using the predicted alpha and beta counting efficiencies 27% and 52%, respectively, of the instrument under improved conditions.

In the case of natural radon concentrations in air, calculations were based on the fact that the sampling interval exceeds three hours which gives sampling equilibrium and the samples are counted immediately after sampling. At equilibrium value the rate of deposition of radioactive daughters of radon is equal to the rate of decay of the activity.[4] These conditions make the counted activity dependent on the sampling flowrate and independent of the sampled volume.

The radioactivity analyzer is sensitive to atmospheric concentrations which are well within recommended maximum permissible levels in air,[8] *i.e.*, 10^4 μμc/m³ for radon-222 and daughters, and 10^2 μμc/m³ for artificial beta radionuclides. Since net counting rates as low as 25 cpm (alpha) and 65 cpm (beta) give good counting statistics (approx. ±10% for 15 minute counting interval), they can be taken as the limits of sensitivity. The corresponding sensitivities for alpha and beta concentrations are in the order of 35 μμc/m³ and 18 μμc/m³ for high flowrates (16.7 liters/min) and low volume (3 m³) sampling, respectively.

Summary

A prototype mass loading and radioactivity analyzer for atmospheric particulates was developed. Beta gauge technique utilizing carbon-14 is applied to measurement of the thickness of particulate deposits collected on membrane tape. This technique for mass loading analysis is also applicable to paper tape and other media of comparable thickness. The result is expressed in terms of concentration values, *i.e.*, micrograms of particulate per cubic meter of air (μg/m³). The proportional counter in the instrument also

measures the alpha and beta radioactivity content of the dust deposit and the concentration values are in terms of micro-microcuries of activity per cubic meter of air ($\mu\mu c/m^3$).

Preliminary indications are that mass loading analysis can be made of particulate concentrations within 100 $\mu g/m^3$ but additional empirical data will be required to assess the effect of combined errors before the limit of sensitivity can be established. Concentrations of natural radioactivity by alpha detection can be measured as low as 35 $\mu\mu c/m^3$, and artificial radioactivity concentrations by Beta detection at 18 $\mu\mu c/m^3$, both values being well within recommended maximum permissible levels in air.

Present semi-automatic operation of the instrument permits rapid analyses of a series of samples on tape. Work is currently underway on indicated improvements to increase the sensitivity of the instrument and automatically record the data as the analysis is performed.

Acknowledgment

The authors express their appreciation to their staff member, Mr. Charles Norris, electronic technician, for his helpful assistance in the development of this instrument and the related experimental work.

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Radiological Health Data

THE DEPARTMENT OF HEALTH, Education, and Welfare has announced the issuance of a new monthly technical publication giving levels of radioactivity in air, water, milk, and other elements of our daily environment. This publication is an outgrowth of President Eisenhower's directive to the Department to "intensify its radiological health efforts and have primary responsibility within the executive branch for the collation, analysis, and interpretation of data on environmental radiation levels." Entitled *Radiological Health Data* this publication is compiled from a number of sources by the Public Health Service's Division of Radiological Health with the assistance of a board of editorial advisers representing the Departments of Health, Education, and Welfare; Defense; Agriculture; and Commerce; and the Atomic Energy Commission.

The first issue appeared in April 1960 and gives data on strontium-90 in milk collected at various places and times throughout this country. Similarly reported are the radioactivity levels in air and water. The price of the publication is 50 cents per single issue and $3.00 for a 6-month subscription from the Office of Technical Services, U.S. Department of Commerce, Washington 25, D.C.

A Survey of Results of Investigations on Some Organic Mercury Compounds Used as Fungicides

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HIGHLY toxic organic mercury compounds are nowadays used more and more as fungicides in agriculture, the paper industry, and the textile industry. As early as 1865 Edwards[1] described the classical picture of poisoning with alkyl mercury compounds (below called Alkyl-Hg). This picture has later been described in more detail by several authors.[2-5]

Symptoms of Poisoning

The picture of the disease is dominated by symptoms and signs from the central nervous system. This is in sharp contrast to poisoning with inorganic mercury salts where renal damage is the main injury. Symptoms and signs of poisoning with phenyl mercury compounds (below called Phenyl-Hg) are less well known.

The symptoms of poisoning with Alkyl-Hg are, with increasing severity of the disease: fatigue, headache, impairment of memory and concentration, numbness and tingling of lips and tongue, and later also of fingers and limbs, slurred speech, ataxia and impairment of gait. There may be concentric narrowing of the visual fields and impairment of hearing. The symptoms may develop with a latent period of several weeks. In a given case, the symptoms may develop to a certain degree and later either remain unchanged, or decrease more or less.

It is important to note that signs of renal damage are of minor importance and that severe renal injury with anuria and uremia does not belong to the picture of poisoning with Alkyl-Hg.

Toxicity and Mode of Action

The acute toxicity of the different Alkyl-Hg, Phenyl-Hg and inorganic salts is about the same when administered parenterally or by mouth to animals.[6, 7] Clinical experience, however, indicates that the risk of poisoning is greater from Alkyl-Hg. This may partly be explained by the higher volatility of Alkyl-Hg,[8] but other factors may also be of importance. After administration of equal amounts of mercury as Alkyl-Hg, Phenyl-Hg or corrosive sublimate, the mercury is excreted in the urine at a much slower rate when administered as Alkyl-Hg and thus the risk of accumulation is greater.[9, 10]

It is a common opinion that the organic mercury compounds, here discussed, on account of their solubility in fat, would have a special affinity for the central nervous system. We, too, were of this opinion formerly[5] but we have later found it not to be valid. In animal experiments, there is always a comparatively low content of mercury in the brain, always lower than in the blood. The concentration, in the range of doses applied, is proportional to the concentration in the blood. The ratio between the mercury content of the brain and the blood is somewhat lower for Alkyl-Hg than for Phenyl-Hg and seems to be highest for inorganic salts.[10, 11] As the excretion of Alkyl-Hg is slower than the excretion of Phenyl-Hg and inorganic salts, at least as long as there is no kidney damage, there is a possibility for the accumulation of high concentrations of Alkyl-Hg in the blood from repeated exposures to small amounts. At the same time, the concentration of Alkyl-Hg in the brain increases and possibly reaches a level high enough to cause damage to the cells and symptoms of poisoning.[10]

Incidentally, it is of interest to note that whereas inorganic mercury compounds in the blood are transported mainly in the plasma the Phenyl-Hg and Alkyl-Hg are bound mainly to the erythrocytes.[9]

Therapy

Contrary to experience from the treatment of poisoning with corrosive sublimate, there is no therapeutic effect from BAL in experimental Alkyl-Hg poisoning.[12] On the contrary, the condition may get worse if BAL is given in the acute stage of poisoning. The administration of BAL in experimental poisoning does not influence the content of mercury in the tissues.[14]

Presented at Twenty-First Annual Meeting of the American Industrial Hygiene Association, Rochester, New York, April 25-28, 1960.

BAL administration may possibly be of value in treating sequelae of Alkyl-Hg poisoning.[5, 12] In these cases there may be some inorganic mercury left in the tissues that may be removed and excreted.

Field Investigations

As there have been some cases of poisoning from Alkyl-Hg in Sweden, we have undertaken large field investigations to study the possibility of safely using the substance. We have examined groups of employees and determined the excretion of mercury in the urine, since we had found in animal experiments that mercury appears in the urine immediately after its introduction into the body[9] and that there is a continuous excretion for several weeks. Mercury was determined with a conventional dithizone method.[5]

A factory producing Alkyl-Hg. When the investigation was started the plant was old and the hygienic conditions poor. Accordingly, the excretion of mercury was found to be high (cf Figure 1). It was, however, not possible to determine how much of this mercury in the urine was due to exposure to metallic mercury and how much to exposure to Alkyl-Hg. The employees were exposed to both. Later the plant was renovated and, as a result, the exposure of the employees decreased. However, the excretion was still considered to be too high, especially as we could not tell the proportion of exposure to vapors of Alkyl-Hg and of mercury metal. If the excretion was due to exposure only to Alkyl-Hg this excretion in the urine could not be tolerated. Thus the conditions had to be improved still more. We now used the excretion of mercury of the human samplers as a guide for further improvements of different steps in the production, which became highly mechanized and enclosed. The workers were protected by air line masks, rubber gloves, rubber clothes, etc. As may be seen from Figure 1 there was a steady decrease in the excretion of mercury. During recent years the excretion has decreased still more.

A thorough clinical examination of these employees has not revealed any signs of damage.[16] From this investigation it is clear that even large quantities of Alkyl-Hg can be handled safely.

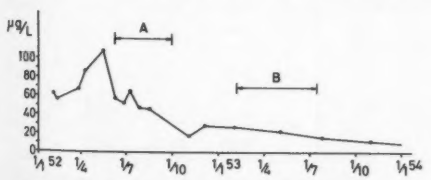

FIGURE 1. Mercury excretion of employees in a factory producing alkyl mercury compounds. A: Period of rebuilding. B: Period of improvement of different steps of production.

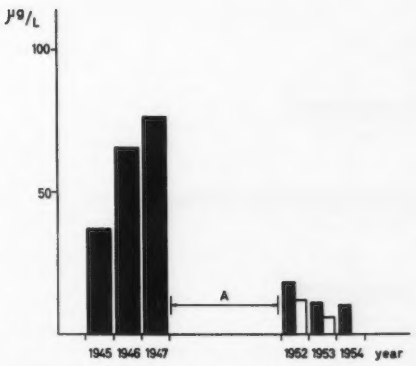

FIGURE 2. Studies on a seed dressing station. Urinary excretion of employees at the end of the season. A: Indicating reconstruction of the station.

Seed dressing stations. Figure 2 shows the results of a similar control of the workers of a very big seed dressing station. Here, too, the results of the urine analyses were used as a guide for the reconstruction of the station, and following improvement of the hygienic conditions, the mercury excretion of the employees has decreased to a permissible level. When studying these results it is worth mentioning that the amount of seed treated during the period after the reconstruction increased several times as compared with the earlier period. Before the reconstruction there had been recorded cases of poisoning but afterwards there have been no complaints. Thus the material can be handled safely here, too.

Figure 3 shows the results of a similar investigation on a group of other seed dressing stations.[17] It is evident from this figure that the equipment used for the procedure determines the degree of exposure. Most stations have good closed machines with a mechanical exhaust system. Practically all small stations had machines of this type.

In no case did we find any symptoms of poisoning. As the excretion of mercury of the employees examined was low as a rule, we consider it possible to do seed dressing safely if suitable equipment is used.

Farmers doing their own seed dressing. The farmers often work under very primitive conditions. They must be exposed to relatively high concentrations of Alkyl-Hg in the air. The time of exposure is, however, very short, only part of a day or two each season, and thus the total exposure may be within tolerable limits as is also

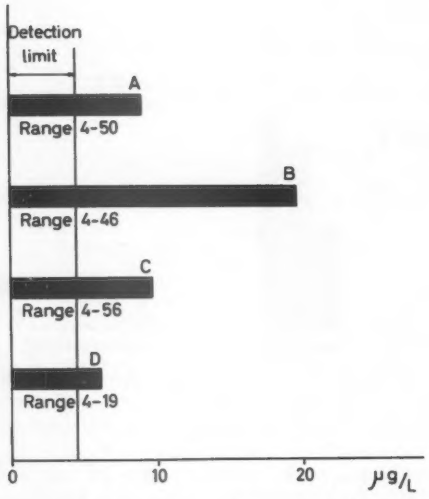

FIGURE 3. Average urinary excretion of mercury in different groups of workers handling alkyl mercury compounds. A: Big seed dressing stations with good equipment. B: Big seed dressing stations with inadequate equipment. C: Small seed dressing stations. D: Farmers.

indicated by a low excretion of mercury in the urine.[18] None of these individuals revealed any symptoms of poisoning.

Seed control stations. We have examined the employees of our biggest seed control station, where samples of treated seed are handled and examined. We found nothing indicating that the handling of these samples would be hazardous. Now and then small samples of seed are treated with a mercurial compound and this of course must be done with due precautions.[4]

Paper industry. In the paper industry Phenyl-Hg is used to a considerable extent as a fungicide and some experiments have been done with Alkyl-Hg.[19] In field investigations in connection with the introduction in Sweden of Phenyl-Hg in the paper industry we found the average exposure to be very low. Only employees directly handling the preparations showed any excretion of mercury in the urine.[20]

In later investigations it has been shown that the mercury in the atmosphere of the factory using Phenyl-Hg or Alkyl-Hg is metallic vapor resulting from decomposition of the organic compound.[19] It seems possible to eliminate any risk in connection with the use of organic mercury compounds in the paper industry by careful handling of the substance.

Determination of Mercury Vapors in Air

An investigation in a factory producing Phenyl-Hg and a paper factory showed that some employees now and then excreted mercury in the urine and sometimes the values were very high without any signs of poisoning. A thorough examination of the working conditions revealed that they had been exposed to vapors of mercury metal from decomposed Phenyl-Hg, which is very easily decomposed. As the significance of a given amount of mercury in the urine is dependent upon whether it is the result of exposure to the organic compound or to mercury metal it became necessary to find a method of determining these vapors separately. Lindstrom has worked out such a method based on the use of a Kruger Ultraviolet Photometer.[21] With this instrument the vapor of mercury metal is determined directly. The organic compounds are decomposed in a furnace and the total amount of mercury in the air is determined. The difference between the two determinations gives the amount of vapors of organic mercury compounds.

This method has been used, for example, in a study of the hygienic conditions in the paper industries using Phenyl-Hg and Alkyl-Hg.[19] It has been used also to study different mercury compounds used as fungicides in agriculture. Figure 4 demonstrates the decomposition of the vapors of different liquid preparations contain-

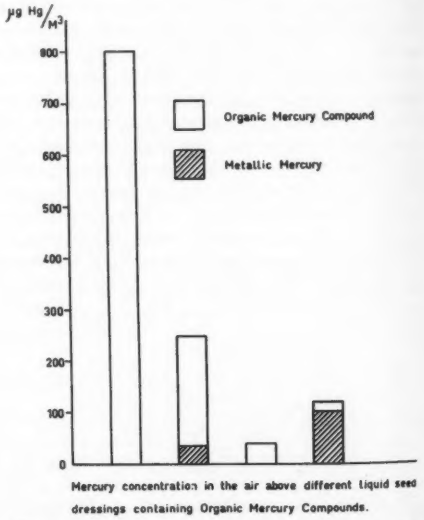

FIGURE 4. Composition of vapors above liquid preparations containing different organic mercury compounds.

ing organic mercury compounds.[22] It has also been used in studying the vapors given off by treated seed.[5] The significance of the amount of mercury excreted in the urine is of course different if it is caused by inhalation of metallic mercury vapors or Alkyl-Hg vapors. We think that this may explain some of the contradictions of the literature.

A modification of this method can be used for the determination of mercury in the urine.[19] The procedure is simple, very rapid and requires but very small amounts of urine. The results have been checked against the conventional dithizone method and are in good agreement. Only 5–10 cc of urine is required for the determination which is completed in a couple of minutes.

For the time being it is not possible to determine in man both inorganic and organic mercury compounds in blood and urine, a distribution that would be of utmost importance.

Conclusions

Summarizing, it may be emphasized that the symptoms of poisoning with Alkyl-Hg are quite different from the symptoms, for example, of poisoning with corrosive sublimate. The toxicity of different organic mercury compounds used as fungicides is roughly the same. Nevertheless the risks are greater in connection with Alkyl-Hg than with Phenyl-Hg depending on differences in volatility and behaviour within the organism. The excretion of Alkyl-Hg is slower, thus allowing the possibility of accumulation. In spite of this, it has been shown to be possible to handle these substances safely.

Determination of the excretion of mercury in the urine of the employees and of the content of mercury in the air is a valuable aid in controlling the hazard and guiding technical improvements.

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Determination of Decaborane by Means of Ferricyanide

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THE GREAT reducing power of the boranes has been utilized in the development of appropriate analytical methods for these interesting and, unfortunately, so toxic materials. The first method[1] uses the reduction of phosphomolybdic acid to the well known blue complex, and the second one[2] employs triphenyltetrazolium chloride, which is reduced by boranes to the bright red formazan, the reduced form of the reagent.

With a view to providing additional methods of borane analysis, that would give the industrial hygienist a greater variety to choose from, the Prussian Blue reaction was investigated. The underlying thought was that it should be possible to reduce ferricyanide to ferrocyanide by means of the borane to be determined, and to react the ferroycanide thus formed with a ferric salt to yield Prussian Blue which in turn would be evaluated by means of colorimetry.

It was recognized from the beginning that the colloidal nature of Prussian Blue would require a careful balance of a number of factors that might influence the size of the colloidal particles. Many difficulties were, indeed, encountered in this investigation, with respect to the choice of reagents, their concentrations, and the operating conditions, but a reasonable method was not evolved until it was realized that light had a striking effect on some of the reagents and perhaps even on the reaction or its product. It was found necessary to carry out operations in subdued light, or even in the dark room, to use actinic glass for the Erlenmeyer flasks in which the reactions were carried out, to keep the reagents in brown bottles, and to let the blank solution "age" for about 24 hours before use. If these precautions were observed, straight line standardization curves and useful results were obtained.

Presented at the Twenty-First Annual Meeting of the American Industrial Hygiene Association, Rochester, New York, April 25-28, 1960. The work reported in this paper was sponsored by the Medical Laboratories of the Army Chemical Center, and by the Callery Chemical Company under a contract from the Bureau of Aeronautics, Department of the Navy.

The method in its present state of development is carried out as follows:

Reagents:

0.05% $K_3Fe(CN)_6$—Store in brown bottle, can be used fresh or old.
0.05% $FeCl_3$ in 0.01*N* HCl—Store in brown bottle, can be used fresh or old.
blank solution—10 ml 0.6*N* NaOH (or equivalent of other concentration).
10 ml ethanol per liter of distilled water—allow to stand for 24 hours before using to ensure complete equilibrium.

Glassware:

Glass stoppered Erlenmeyer flasks, 125 ml—preferably actinic glass. Erlenmeyer flasks are wrapped with aluminum foil to protect against light, unless they are of actinic glass.
Coleman cuvettes—rubber stoppered.

Time Schedule for Solution of Decaborane:

Minutes	Operation
0	0.0282 gram decaborane dissolved in 10 ml of 0.6*N* NaOH and 10 ml of ethanol—mixture swirled.
10	mixture diluted to 1000 ml with distilled water—mixed thoroughly.
15	dilutions made to desired levels, using blank solution instead of distilled water—solutions mixed thoroughly.
25	2 ml of each dilution pipetted into Erlenmeyer flasks in preparation for the Prussian Blue reaction.

Time Schedule for Reaction:

As soon as the dilutions of the original decaborane solution have been completed, the following steps should be taken.

Minutes	Operation
0	2 ml of $K_3Fe(CN)_6$ solution added to each Erlenmeyer containing diluted decaborane solution—mixed for one minute.

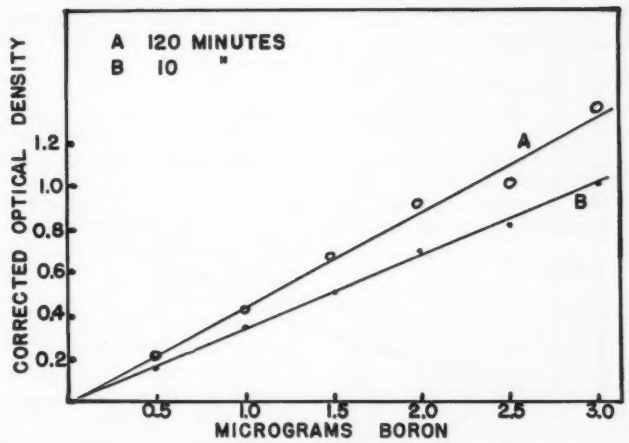

FIGURE 1. Prussian Blue reaction for determining decaborane—influence of reaction time.

10 6 ml of $FeCl_3$ solution added—mixed for one minute.

20 sample read at 675 millimicrons against water, only once; optical density readings taken and correction made for the optical density of the blank before a graph is plotted or readings of unknowns are made from a standard curve.

Figure 1 shows typical standardization curves at two time intervals.

As in many other color reactions, such as the phosphomolybdic acid method for boranes, color development with the ferricyanide method does not readily come to steady state, if it ever does. Borane odor has been observed for as much as two hours, but seemingly the reaction is proportional to the amount of borane present, in the concentration ranges covered by this method. Figure 1 shows the influence of time on color development, and the corresponding figures are given in Table I. This table shows also that an "unknown" decaborane solution, calculated to contain 1.25 micrograms boron per ml, could be evaluated correctly no matter whether the mixture of decaborane solution and ferricyanide solution was allowed to react for 10 or for 120 minutes before developing the color with ferric chloride. The important point is to take one reading at the allotted time and let it go at that.

The influence of aging the blank solution was discovered quite accidentally. In an effort to discern, if possible, other factors that might influence the performance of this method, a sizeable number of tests were made just to amass data. They were run on a uniform basis of operation, *i.e.*, the reaction flasks were covered to shield against light influence, and a reaction time of 10 minutes was allowed before the ferric chloride was added. In plotting the results, it was observed that they could be grouped in two categories: those obtained using blank solutions that had aged about 24 hours, and those obtained using freshly prepared blank solutions. With aged blank solutions, the points for various concentrations fell on substantially straight lines, but

TABLE I

Prussian Blue Reaction: Influence of Reaction Time and Analysis of Unknown Sample

Sample, micrograms boron	Optical density	Corrected O. D.	Micrograms B from curve
Deca and $K_3Fe(CN)_6$ mixed 10 minutes before $FeCl_3$ added:			
Blank	0.030	0.030	
0.5	0.188	0.158	
1.0	0.371	0.341	
1.5	0.535	0.505	
2.0	0.719	0.689	
2.5	0.845	0.815	
3.0	1.061	1.031	
unknown	0.467	0.437	1.28
unknown	0.454	0.424	1.26
Deca and $K_3Fe(CN)_6$ mixed 120 minutes before $FeCl_3$ added:			
Blank	0.030	0.030	
0.5	0.243	0.213	
1.0	0.459	0.429	
1.5	0.695	0.665	
2.0	0.936	0.906	
2.5	1.061	1.031	
3.0	1.383	1.353	
unknown	0.580	0.550	1.27

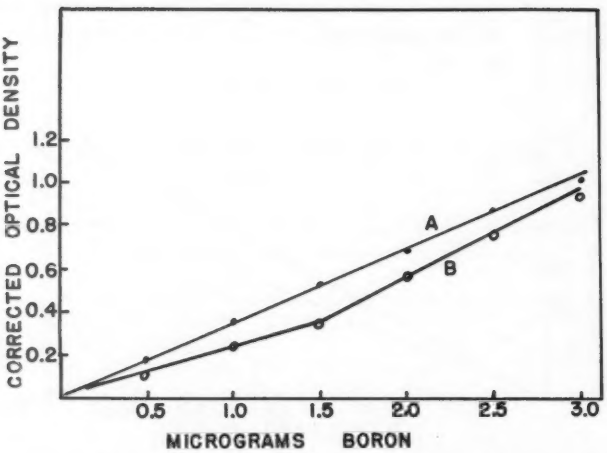

FIGURE 2. Prussian Blue reaction for determining decaborane—influence of aging blank solution. Curve A is the aged blank solution. Curve B is the fresh blank solution.

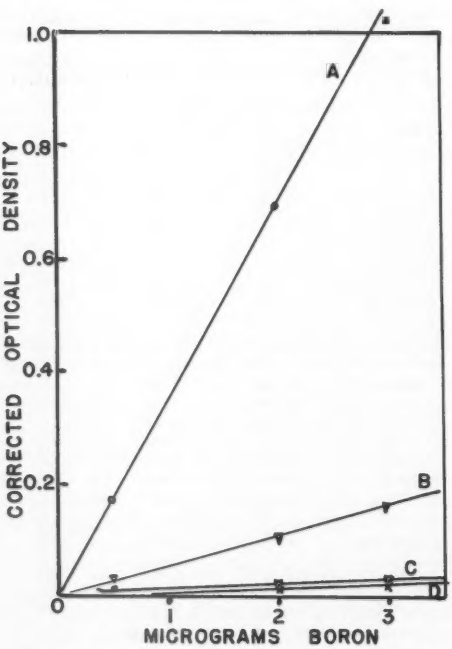

FIGURE 3. Prussian Blue reaction applied to several boranes. A, decaborane; B, pyridine-borane; C, triethylamine-decaborane; D, dimethylamine-borane.

for fresh blank solutions, the lines were decidedly curved or had kinks in them. This was true for the individual tests as well as for the calculated averages. Moreover, it was observed that a fresh blank solution that had been used for a test and had yielded a poor curve would yield a good straight line in an equivalent test the following day. Figure 2 is representative of the curves obtained, and averages were used in plotting them.

While the method was developed for decaborane, its possible applicability to the analysis of other boranes was not ignored. A further point of interest was derived from the work on the correlation of the toxicity of the boranes with their reducing power[3] in which phosphomolybdic acid was employed. It was thought that the borane-ferricyanide system might lead to similar correlations. For this reason, the ferricyanide reaction was applied to dimethylamine-borane, pyridine-borane and triethylamine-decaborane. The general procedure followed was the one given above with these exceptions: distilled water only was used for dissolving dimethylamine-borane, and water was used for making all dilutions. In the case of pyridine-borane, the material was dissolved in 10 ml of propylene glycol, made up to one liter, diluted with the same solvent-water mixture, and the blank solution was prepared in an analogous manner. For triethylamine-decaborane, only NaOH was used for dissolving etc. and no ethanol was added. Dilutions and blank solution were made in like man-

ner. All solutions were aged sufficiently to give color stability. The results obtained are shown in Figure 3 and are compared to a typical decaborane curve.

It will be seen from the figure that the reaction of these borane adducts with ferricyanide is very slow and that not much color is produced. The results also show that in the Prussian Blue reaction, the compounds evaluated do not fall into the same location on the graph relative to each other as had been observed for the phosphomolybdic acid reaction,[3] and that seemingly a correlation with the toxic properties of the compounds does not exist. However, these results are not unequivocal as far as the potentialities of the ferricyanide method is concerned, because this compound exerts its oxidative power under acid as well as under basic conditions of operation so that there remain plenty opportunities for further research which conceivably might produce quite different results.

The main virtue of the ferricyanide method is its great sensitivity which may make it applicable where others fail. It is, of course, nonspecific like the other reduction methods and must, therefore, be used with an equal amount of common sense. The present work is reported at this time, even though it is not regarded to be complete, because we do not anticipate doing more work in this field for the time being but feel that the method should be made available to industrial hygienists.

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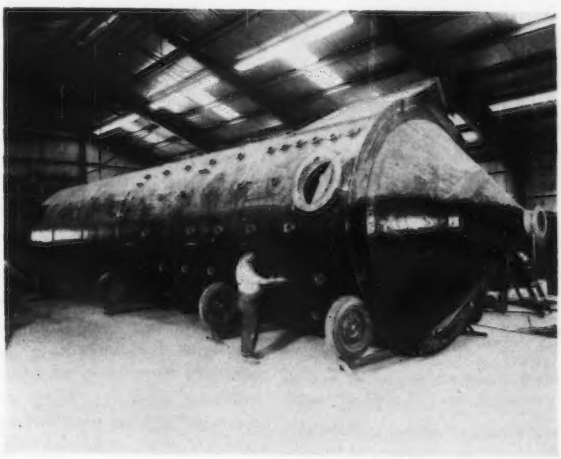
Fume Scrubber

THIS FUME SCRUBBER designed by Buffalo Forge Air Cleaning Division is believed to be the largest unit of industrial equipment ever fabricated from reinforced plastic. Over 47 feet high and 10 feet in diameter, this scrubber is constructed of Hetron® 92, a fiberglass-reinforced polyester plastic of the Hooker Chemical Corporation and will effectively handle 42,000 cfm of severely corrosive fumes, mists and dusts of fluoride compounds. Almost 150 individual spray nozzles are utilized in this apparatus.



Developments in the Measurement of Atmospheric Sulfur Dioxide

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Introduction

SAMPLING, analytical, and standardization procedures used in measurement of sulfur dioxide in the air pollution study conducted by the U. S. Public Health Service in Nashville, Tennessee are described in this paper. The study was conducted with the cooperation of the Tennessee Department of Public Health, the Davidson County Health Department, the City of Nashville, and other Nashville groups. Other work done in this community study will be reported at a later date.

Three methods used in measurement of sulfur dioxide were the lead peroxide candle method developed by the British,[1, 2] the sodium tetrachloromercurate (TCM) method of West and Gaeke[3] adapted to use with an automatic analytical instrument,[4] and a Thomas Autometer.[5, 6] These three methods were used in parallel throughout the study which started in July, 1958 and ended July 30, 1959. In addition, the hydrogen peroxide method as used by Greenburg and Jacobs[7] was used for several months.

Lead peroxide candles were located at 123 sampling sites uniformly spaced over a nine-mile diameter urbanized area. At 36 of these sites, 24-hour air samples also were collected and analyzed using the TCM method. At seven of the 36 sites, two-hourly samples were taken using an automatic sequential sampler.[8] Each sequential sampler collected twelve air samples per day for sulfur dioxide determination using the TCM method. The Thomas Autometer was operated continuously at one of the seven stations.

Sodium Tetrachloromercurate Method

Sampling Procedure

The TCM sulfur dioxide system (Figure 1) was operated at seven sites and was housed in a small building located adjacent to a utility pole. Critical vacuum was maintained on the pump side of flow limiting orifices, thus providing a known constant flow of air. To remove particulate matter air was first passed through a piece of number four Whatman strip filter paper.

On the sequential sampler side of the system, (left hand part of Figure 1) sulfur dioxide was collected by the scrubbing action of 15 milliliters of 0.1 molar sodium tetrachloromercurate contained in midget, fritted bubblers, using an air flow rate of one liter per minute. The twelve midget bubblers were attached to a common intake manifold in the midget bubbler box, and each bubbler side arm was attached to its corresponding solenoid valve of a sequential timer box. The bubbler box (Figure 1) also was used as a carrying box to expedite transportation and bubbler changing procedures. A vacuum was maintained on the pump side of the sequential timer, and the time controlled valves selected the bubbler through which air was passed.

The 24-hour sulfur dioxide samples were collected by the scrubbing action of 75 milliliters of 0.1 molar sodium tetrachloromercurate contained in large, fritted bubblers, using an air flow rate of 0.5 liter per minute (right hand part of Figure 1). An additional one liter per minute orifice in this side of the system provided a total flow of 1.5 liters per minute through a piece of #4 Whatman strip filter paper. This filter was used to determine "soiling power" of atmospheric particulate matter. Change in light transmission through the filter was measured by use of a photometer.

The 24-hour sampler side of the system (right hand part of Figure 1) was employed separately at 29 sites, 25 of which were housed in boxes located eleven feet from the ground on cross arms installed on utility poles. Four of these samplers were used as controls, or background pollution samplers. They were housed in small buildings located on the four major axes of the compass from downtown Nashville and about three miles outside the heavily urbanized area.

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The sampling probe and scrubbing systems (Figure 1) were checked for accuracy by simulating field arrangement of apparatus and then sampling synthetic mixtures of sulfur dioxide and air produced in a 4.1 cubic meter stainless steel chamber. These synthetic mixtures, ranging from 0.5 to 1.5 part per million sulfur dioxide, were produced by charging a syringe with a calculated amount of 100 per cent sulfur dioxide, which was purged into the chamber. This sulfur dioxide-air mixture was then thoroughly mixed. It was found that the stainless steel chamber could be used as a standard if it were first conditioned for four hours with sulfur dioxide concentrations approximating those to be used in the study, then flushed with fresh air, and a fresh, measured mixture produced. Only one TCM result varied as much as ten per cent from the expected theoretical sulfur dioxide-air mixture (Table I).

Three bubblers were placed in series and ten separte runs revealed no sulfur dioxide in the second or third bubblers. Parallel and independent work by McCaldin and Hendrickson[9] and West and Gaeke[3] confirms the finding that the bubblers used are substantially 100 per cent efficient in collecting sulfur dioxide under the conditions of use in this study.

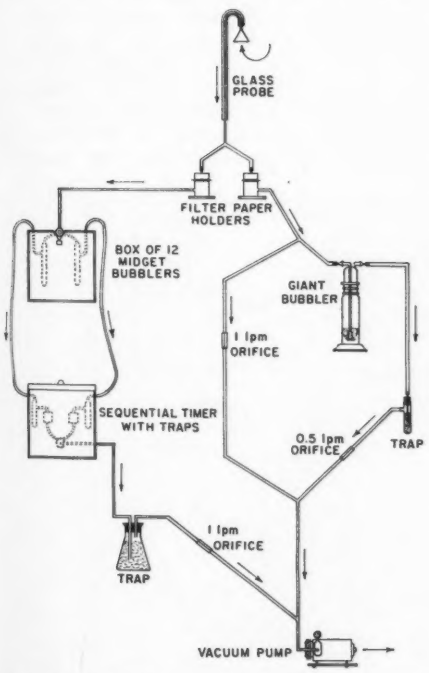

FIGURE 1. Two-hour and 24-hour sulfur dioxide sampling arrangement.

TABLE I
Theoretical and Measured Sulfur Dioxide Concentrations in a Stainless Steel Test Chamber

Sample No.	Theoretical mixtures ppm	TCM results ppm
1	1.0	0.90
2	1.0	0.96
3	1.0	1.08
4	0.5	0.48
5	1.0	0.97
6	1.5	1.55

During this phase of the study, it was determined that a ten foot long sampling probe of fresh Tygon tubing would retain from 24 to 64 per cent of the sulfur dioxide from a one part per million synthetic mixture flowing at a rate of one liter per minute. This agrees with findings of Patterson, *et al.*,[10] and of McCaldin and Hendrickson.[9] Undoubtedly the tubing would reach a state of equilibrium with respect to retention of sulfur dioxide. However, the time required to reach equilibrium and the effect of intermittent use were not known. Therefore glass sampling lines were used.

It was known that some of the samples would have to be held in the field and laboratory for up to seventy-two hours before being analyzed. A study of results from a series of sulfur dioxide samples (aliquots from samples just taken, versus aliquots from the same samples analyzed 24 to 72 hours later) revealed that there were no statistically significant differences between sets of data. Therefore, over the range of concentrations used in this experiment, it can be said that the disulfitomercurate formed with the TCM method is stable up to at least seventy-two hours after sampling (Table II). McCaldin and Hendrickson[9] found an average decrease of one per cent per 24-hours over a holding period of 21 days, *i.e.*, three per cent for 72 hours.

There was concern that there might be a change in composition and/or contamination of the collecting medium on standing in the field and laboratory. This was investigated by placing two control samples (fresh collecting medium in midget bubblers) alongside the routine sampling bubblers at two of the sampling sites. This study was carried on for a month. The control samples did not differ from freshly made-up collecting medium, indicating there was no decomposition or contamination of the sodium tetrachloromercurate under the conditions of use in the Nashville study.

Midget Bubbler Handling

On reaching the laboratory, three milliliters of the sample were poured through the vacuum side-arm of the bubbler into a sample cup. The bubblers were cleaned without disassembling by use of a special cleaning apparatus (Figure 2). The used collecting medium was pulled out through the bubbler stem by vacuum. Distilled water was drawn, by vacuum on the bubbler stem, down through the bubbler cylinder and out through the stem. The apparatus made it possible for a person to wash 84 bubblers in 15 minutes with about one-twentieth of the amount of distilled water involved in manual washing. Breakage of midget bubblers was minimized. Cleaned bubblers were charged with new sampling medium by slipping the top of the bubbler stem up into a rubber tube connection on a vacuum-filled, fast-flow burette (Figure 2). The system controlled a potential mercury hazard to workers which could have resulted from both skin contact and hand-to-mouth ingestion, in addition to saving manpower.

TABLE II

Stability of Sulfur Dioxide Samples with Respect to Storage Time

Sample No.	Micrograms sulfur dioxide per ml of TCM reagent after stated number of hours of storage			
	0	24	48	72
1	5.2	5.1	5.0	5.1
2	5.2	5.2	5.1	5.2
3	5.2	5.1	5.2	5.1
4	5.5	5.2	5.1	5.1
5	3.0	3.0	2.7	3.0
6	3.0	2.9	2.7	2.7
7	2.7	2.7	2.5	2.7
8	2.5	2.5	2.3	2.4
9	2.5	2.7	2.3	2.5
10	2.5	2.5	2.3	2.4
11	2.5	2.7	2.6	2.6
12	2.5	2.6	2.5	2.5
13	1.3	1.3	1.3	1.3
14	1.4	1.4	1.4	1.4
15	1.4	1.4	1.3	1.4
16	1.4	1.4	1.4	1.4
17	0.8	0.9	0.9	0.9
18	0.9	0.9	0.9	0.9
19	0.8	0.8	0.8	0.8
20	0.9	0.9	0.9	0.9

Adaptation to Automatic Colorimetric Analysis

Accomplishmenrt of the laboratory workload of analyzing 120 samples taken each day, seven days a week, was made feasible by adaptation of the TCM method to use with an automatic analytical instrument.[4] The instrument is simple in principle and was operated for over a year in the Nashville study with a minimum of maintenance problems.

A portion of each sample was poured into a three-milliliter polystyrene cup and placed on a timed turntable, which indexed each cup in turn to position under a sampling probe. The probe was raised every minute and a half, during turntable rotation. When the probe was raised, air was sucked in which acted as a barrier between samples as they flowed along the analyzing

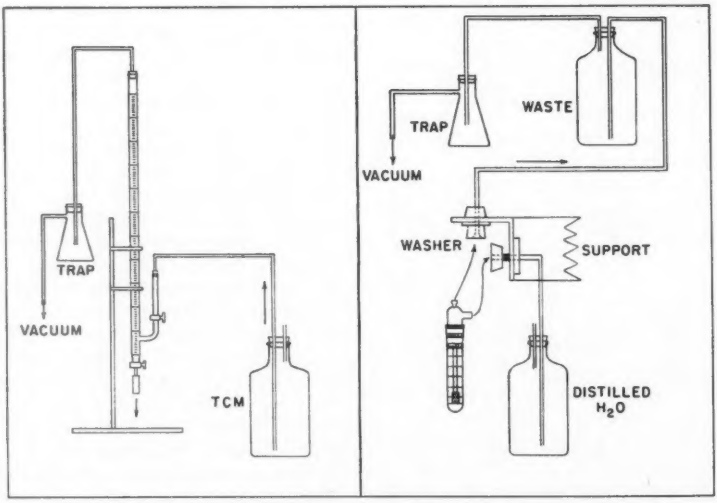

FIGURE 2. Midget bubbler washing and charging apparatus.

route. The probe was then dipped into the next cup after the turntable was indexed. By the stripping action of a roller proportioning pump upon four different-diameter plastic tubes, known amounts of sample and reagents were simultaneously picked up and pushed through a glass mixing coil. The three reagent tubes picked up proper quantities of 0.2 per cent formaldehyde; a mixture of 0.005 per cent pararosaniline hydrochloride and 5 per cent hydrochloric acid; and a 0.1 molar sodium tetrachloromecurate solution. These three reagents and the sample came together in a common mixing coil to form a quantitative red-violet color. The sample and reagent mixture was moved continuously through to a colorimetric flow cell where air bubbles were released. The color change was plotted in percentage transmission on a strip chart recorder.

Using the automatic instrument, it was possible for one person to analyze about 36 samples per hour. The procedure does not require manual sample or reagent measurement. Color development time is automatically standardized by the instrument. These factors reduced the operative error to a minimum and allowed change in personnel without affecting the quality of results.

The only major dlifficulty encountered in adapting the TCM method to use with the automatic instrument was a dye build-up in the mixing coils which caused high and erratic results. This was remedied by diluting the dye concentration from 0.04 per cent pararosaniline and 6 per cent hydrochloric acid, as recommended by West and Gaeke, to 0.005 per cent and 5 per cent respectively. The revision still allows sensitivity as low as 0.006 part per million sulfur dioxide with a 120-liter air sample scrubbed through 15 milliliters of sampling solution.

TCM Method Compared to Others

TCM versus Thomas Autometer

The Thomas Autometer was calibrated by the sulfuric acid method normally used. Since it was impracticable to bring the Thomas Autometer to the stainless steel chamber, the relationship between the Thomas Autometer and the TCM method was established by using a Mylar bag as a "chamber" (Figure 3) in the following manner:

(1) Evacuate Mylar bag.
(2) Charge syringe with calculated amount of 100 per cent sulfur dioxide to introduce into 200 liters of air to produce desired gas concentration in bag. This concentration will be higher than that required for the test since the gas mixture from the Mylar bag will later be diluted with more air when running a test.
(3) Charge Mylar bag with 200 liters of air passed through a soda-lime tower. Purge the syringe of 100 per cent sulfur dioxide into air stream during this process.
(4) Connect the equipment as shown in Figure 3 (solid lines). The Autometer pump (A) is used to pull the mixture of sulfur dioxide from the Mylar bag and additional dilution air through the scrubbing

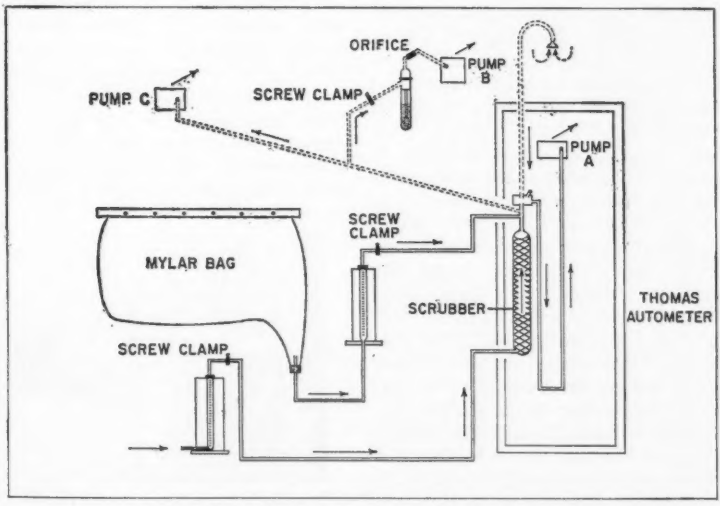

FIGURE 3. Mylar bag dynamic calibration system.

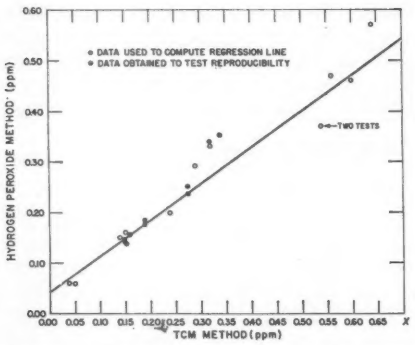
o DATA USED TO COMPUTE REGRESSION LINE
• DATA OBTAINED TO TEST REPRODUCIBILITY
o—o TWO TESTS
HYDROGEN PEROXIDE METHOD (ppm)
TCM METHOD (ppm)
0.00 0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45 0.50 0.55 0.60 0.65 X
0.00 0.10 0.20 0.30 0.40 0.50 0.60

FIGURE 4. Relationship between sulfur dioxide concentrations measured by TCM and hydrogen peroxide methods.

tower in place of normal outside air. This is done by positioning a glass T valve. Dilution ratio is controlled by the screw clamp on the Mylar bag air line and is computed by the ratio of flows in the Mylar bag and dilution lines. The test concentration is the Mylar bag concentration divided by one plus the dilution ratio.

Enough time was allowed for two complete cycles (one hour) of the Autometer. This was done in order to allow enough time for the Autometer to reach equilibrium. After the Autometer had been run on the calibrating gas for one hour, the glass T valve was positioned so that the Autometer returned to normal operation on outside air and the clamp on the Mylar bag line was closed. All of the equipment was left as set up for Autometer calibration, and a glass tube leading to the bubbler was put in the calibration line to replace the Autometer. The sampling apparatus was then arranged as shown on Figure 3 (broken lines). Pumps B and C were turned on and the bleeder valve on pump C and screw clamp on the dilution line were properly adjusted. The Mylar bag line clamp was then opened sufficiently to obtain the correct flow rate and the sulfur dioxide mixture allowed to flow through the system long enough for stabilization. A fresh bubbler was then placed in line and a sample was taken. The bubbler samples were analyzed using the automatic analytical instrument. A theoretical mixture of three parts per million was produced in the bag for this study. The stabilized reading on the sulfuric acid calibrated Autometer was 3.4 parts per million and the value for TCM samples taken immediately after also was 3.4 parts per million sulfur dioxide. Thus the correlation factor between the two methods appears to be unity for mixtures of purified air and sulfur dioxide. However, data for only one concentration level have been used to establish the relationship between the two methods.

TCM vs Hydrogen Peroxide

Correlation between the TCM and hydrogen peroxide methods was established by collecting simultaneously samples from a common probe using small fritted bubblers, one charged with TCM and the other with hydrogen peroxide collecting media. Twelve paired results were plotted (Figure 4) and the line of best fit was determined by the least squares method. The relationship can be expressed as:

$$y = 0.72\ x + 0.04$$

where y is hydrogen peroxide method results and x is TCM method results. The correlation coefficient was +0.88. A re-run of the experiment showed reproducibility to be good (Figure 4).

Lead Peroxide Candle Method

The lead peroxide candle method for the fixation and analysis of sulfur dioxide, as used in the Nashville study, was similar to that described by Parker and Richards,[2] with modifications developed by the Tennessee Valley Authority. Although results obtained by use of this procedure are not yet analyzed, a description of the method used is given here to round out the description of sulfur dioxide methods used in the Nashville study. This method, by the combination of water insoluble lead peroxide on the candle and sulfur dioxide in air to form water insoluble lead sulfate, provides an inexpensive measure of relative sulfation. The lead peroxide candle consists of an 8-ounce round sample jar wrapped with a strip of two-inch gauze bandage, giving an area of 100 square centimeters of gauze. The gauze is painted with a mixture of lead peroxide in gum tragacanth, alcohol, and water (Figure 5). For standardiza-

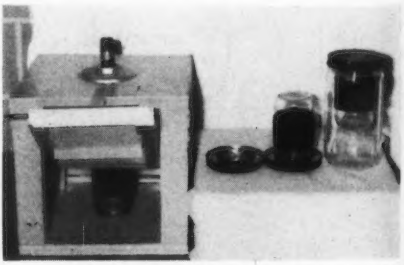

FIGURE 5. Lead peroxide sampler in louvered box and with carrying jar.

tion purposes, sufficient lead peroxide of low sulfate content was purchased in one lot to supply the Nashville Project over the full term of the study.

The metal screw cap from the eight-ounce jar was riveted to the inside of a 32-ounce wide-mouth jar top. After the lead peroxide candle had been made, it was screwed into the 8-ounce jar top attached to the larger top. The jar and tops were then inverted and fitted to a 32-ounce jar. This assembly was used in making transfers and for storage.

Lead peroxide candles were used at 123 stations. They were exposed to the atmosphere for one month in louvered boxes (Figure 5). These were mounted eleven feet above the ground on crossarms attached to electric power poles. One of the requirements in station selection was that there be no obstructions (buildings, trees, etc.) from 45 degrees to 90 degrees above the horizon from the shelter, thus providing for good air movement at the shelter.

After one month's exposure, the sulfate formed was analyzed gravimetrically by the usual barium chloride method and was reported in milligrams of sulfur trioxide formed per 100 square centimeters of lead peroxide surface per day.

Summary

In the course of an air pollution research study in Nashville, Tennessee, the sodium tetrachloromercurate (TCM) method for collection and analysis of low concentrations of sulfur dioxide was found to be accurate, highly sensitive, flexible, and practical. The adaptation of this method to use with an automatic analytical instrument and methods of rapid midget bubbler handling, washing, and filling procedures are described.

The relationship between this modified TCM method and two other methods was investigated, using synthetic mixtures of sulfur dioxide in air. A dynamic calibration procedure showed that Thomas Autometer and the TCM results are identical. The relationship between the hydrogen peroxide and TCM methods was found to be: (H_2O_2 results in ppm) = 0.72 × (TCM results ppm) + 0.04.

The lead peroxide candle method for estimation of sulfur dioxide as used in Nashville is described.

Acknowledgment

The authors wish to express their thanks to the Industrial Hygiene Service, Tennessee Department of Public Health, for the use of the stainless steel chamber.

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Music in the Air

IN THE AMERICAN INDUSTRIAL HYGIENE JOURNAL, December, 1959, we published an article "Calibration of Alnor Velometers" by George Hama. In this he reported using an adventiously obtained sousaphone bell in the calibration assembly. The aerodynamic characteristics of the bell of this horn are so good the entry loss is only 2% of velocity pressure. Another ingenious reader of the Journal has used this item but reports that a sousaphone bell can be obtained more simply than prowling junk yards or hock shops. The Conn Corporation of Elkhart, Indiana in reply to his inquiry, said that they can offer for sale a giant sousaphone bell in an "as-spun" state from brass, without the bell wire. The price is about $15.00 each with delivery in from 30 to 60 days for small quantities.

The Determination of Organic Vapors in Air by Gas Chromatography Using a Direct Injection Method

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GAS CHROMATOGRAPHY has attracted workers in the field of industrial hygiene from the time that this technique was first described in 1952.[1, 2] Although it is especially adapted to the determination of micro quantities of vaporizable organic compounds the use of gas chromatography in the analysis of air-borne contaminants was handicapped by the lack of simple sampling techniques and sufficiently sensitive methods to detect the minute traces found in air samples.[3]

A number of methods have been developed for trace analysis by gas chromatography and in our opinion the work of C. D. Lewis *et al.*[4] is particularly notable. However, gas chromatography of air samples has been clouded by the difficulties which are encountered due to the presence of atmospheric moisture. This was shown clearly by West,[5] who used a cooled, activated carbon adsorbent to trap the traces sought and then dried the desorbed sample by passing it through magnesium perchlorate. Desty[6] sampled on a silicone grease partition trap and used calcium hydride as a drying agent. Eggertson[7] used Ascarite® as a drying agent but pointed out that further study was needed to determine whether the drying agent caused a loss of sample by adsorption. More recently Farrington and associates[8] studied this problem and found that anhydrous sodium carbonate was an efficient drying agent. He found, however, that there was considerable adsorption of oxygenated aliphatics on the anhydrous sodium carbonate. McKee[9] explored the whole problem of losses of air-borne vapors when the sample is dried with the conventional desiccants and favored Ascarite® for air pollution work, noting that it caused the lowest loss.

Our experience showed similar undesirable effects of drying agents on the concentration of vapors in air samples. We, therefore, turned to a simple scrubbing technique using spectrographic grade meta-xylene to trap air-borne vapor contaminants.[10] The same general approach was taken by Mansur,[11] who used a somewhat more detailed technique for the final analysis.

We felt that direct chromatography of the air sample and isolation of moisture by the column itself was a more desirable approach. In 1956 Adlard[12] described the application of the polyglycols to the chromatographic examination of water. Subsequently, Bodnar[13] used a polyethylene glycol (PEG) 400 column to determine traces of organic solvents in water. This liquid phase appeared to offer possibilities and we prepared an 8.5-foot column of ¼-inch copper tubing, using PEG 400 and a solid support of Johns-Manville C-22 firebrick.

The firebrick was crushed with a hammer and then ground. The portion passing through a 40 mesh sieve and retained on 60 mesh (ASTM designation E 11) was selected. This was washed free of fines by successive sedimentation in distilled water and dried at 150°C. The column was prepared according to the Beckman Manual[14] using reagent grade methanol as the solvent for the PEG 400. The ratio of liquid to solid was kept at 1:3.

A column temperature of 94°C gave satisfactory results. The katharometer filament current was kept at 320 ma and the gas flow at 77 cc per minute. These conditions yielded good resolution of ortho- and meta-xylene and have proven to be applicable to this method.

Preliminary runs showed that the column was suitable for the removal of atmospheric moisture (Figure 1). The apparent retention time for water was 36 minutes, permitting the chromatography of most of the common industrial solvents (Table I and Figure 2). The column produced good Gaussian curves for all the organic solvents investigated except water which tended to tail out. Resolution of methyl alcohol and isopropyl alcohol was not good but we believe that this may be improved by varying the physical characteristics of the column. The behavior of methylene chloride was interesting. Al-

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though it has a higher vapor pressure than carbon tetrachloride, it has a greater retention time.

A group of wet and dry standards were prepared to determine if atmospheric and liquid samples of equal concentrations of contaminants would yield comparable data. The liquid standard was prepared by dissolving a weighed amount of carbon tetrachloride in meta-xylene, so that five microliters of solution would be equivalent to an air sample of 50 cc containing

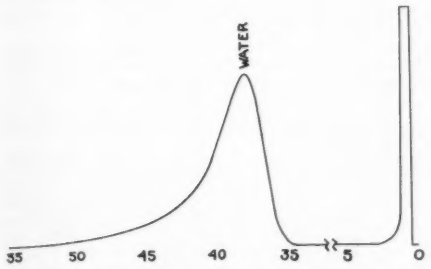

FIGURE 1. Atmospheric water. PEG 400 column; temperature 94°C; helium flow 77 cc/min; filament current 320 ma; attenuation 1; apparent retention time 36 minutes.

TABLE I

Chromatography of Some Common Organic Solvents at 200 PPM Concentration PEG 400 Column

Temperature: 94°C; Helium flow 77 cc/min; filament current 320 ma, instrument attenuation level, 1.

Compound	Wt. of solvent (micrograms)*	Apparent retention time (minutes)	Peak height (millimeters)
Acetone	23.7	5.7	54
Methyl ethyl ketone	29.4	8.5	39
Methyl isopropyl ketone	35.2	10.9	35
Methyl isobutyl ketone	40.9	17.0	28
Methanol	13.1	11.0	21.5
Ethanol	18.8	13.4	20.5
Isopropanol	25.5	12.05	33
n-Butanol	30.0	47.3	11.5
n-Propanol	25.5	24.6	14.5
Ethyl acetate	36.0	7.5	54
n-Butyl acetate	41.7	23.0	18
n-Amyl acetate	53.2	30.6	13
Benzene	31.9	9.4	44
Toluene	37.6	17.0	26
Xylene(meta)	43.4	29.7	19.5
Carbon tetrachloride	62.6	5.8	34
Methylenedichloride	34.8	7.9	47
Trichloroethylene	53.6	11.7	40
Tetrachloroethylene	67.9	14.2	35

* Equivalent to 50 cc air sample containing 200 ppm of solvent.

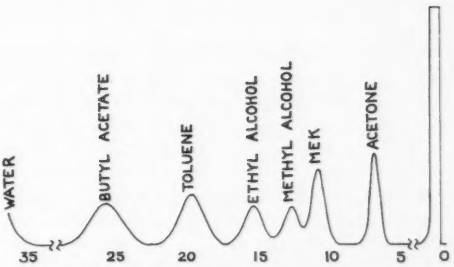

FIGURE 2. Chromatograph of some common organic solvents. PEG 400 column; temperature 94°C; helium flow 77 cc/min; filament current 320 ma; attenuation 1.

TABLE II

Peak Height Measurements of Liquid and Vapor Standards of Carbon Tetrachloride PEG 400 Column

Parts per million	Peak Height (mm)	
	Liquid standard	Vapor standard (50 cc sample)
25	4	4
50	8	8
100	17	16
200	34	33
400	67	65
600	101	98
800	135	131
1000	167	165

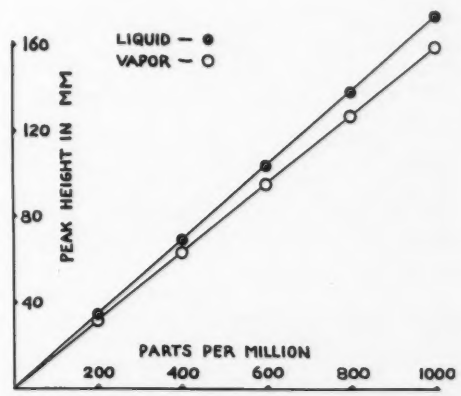

FIGURE 3. Peak height measurements of liquid and vapor standards of carbon tetrachloride. PEG 400 column; temperature 94°C; helium flow 77 cc/min; filament current 320 ma; attenuation 1.

100 parts per million of the chlorinated compound.

The dry standard was prepared in a 46.4-liter glass jug provided with a stirring fan and two sampling ports about 180° apart half-way down the belly. The ports were sealed with serological type rubber stoppers. Concentration of vapor was maintained for periods up to 55 hours without notable loss. Weighed samples of carbon tetrachloride were sealed in glass ampules and attached to the fan shaft with platinum wire. They subsequently were broken by the whirling blades of the fan. After an hour of stirring the air sample was withdrawn from the jug with a 50-cc B & D syringe fitted with a #19 gauge needle and injected directly into the liquid sampling port of the chromatograph. Experience showed a #25 gauge needle created too much resistance to injection and caused losses of sample as high as 10%. Injection was easier with the larger bore needle and though there was some loss of sample it was not objectionable for practical work.

All quantitative measurements were made by the peak height method described by Keulmans.[15] Table II and Figure 3 contain a summary of the data obtained with carbon tetrachloride. Although there is a loss of sample by this method it is not enough to be significant.

Conclusions

The polyethyleneglycol 400 column offers a practical solution to the annoying problem of moisture in the chromatography of air-borne vapors. It permits the application of direct injection of the sample into the column and thus expands the usefulness of this type of analysis for the industrial hygienist. This technique is simple. With a set of standards prepared directly from the solvents themselves, the need for test tank standardization of the chromatograph is eliminated.

By changing the operating conditions of the column, perhaps by modifying it, the sensitivity of this method possibly can be developed to detect much lower levels of traces than we have shown, without the need of resorting to costly detection systems and complicated sampling arrangements.

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Development of a Freeze-out Technique and Constant Sampling Rate for the Portable Uni-Jet Air Sampler

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THE FREEZE-OUT technique for the isolation of condensable atmospheric contaminants is not a new concept.[1, 2] An evaluation of the standard midget impinger used in connection with the Uni-Jet Air Sampler®[3, 4] (Union Industrial Equipment Corp., Port Chester, N. Y.) under these conditions has not been available to investigators in the air pollution field. Therefore, a study was undertaken to determine what modifications were required to adapt the midget impinger for the efficient collection of trace contaminants by low temperature condensation, and what limitations would be encountered in field application.

Long-term air scrubbing, through volatile liquids, leads to the loss of solvent unless vaporization is reduced by cooling. Utilization of the cooling effect of expanding refrigerants led to the development of a constant rate Uni-Jet Air Sampler®. Liquid Freon-12® fed through an automatic back pressure control valve into a vaporizing coil not only lowered the temperature of the coil, but also delivered a constant volume of gaseous Freon-12® with sufficient pressure to produce the desired vacuum at the aspirator.

Procedure

Two representatives of industrial air contaminants were selected for their widely different volatility characteristics and for which reliable standard analytical procedures were available. Nitrobenzene, a high boiling compound (bp- 410°F, vapor pressure- 0.23 mm at 75°F), was determined in an ethanol solution by ultraviolet spectroscopy. Carbon bisulfide, a low boiling compound (bp- 115°F, vapor pressure- 360 mm at 75°F), was determined by the diethylamine-cupric acetate method of McKee.[5]

Standard solutions of nitrobenzene and carbon bisulfide in iso-octane were injected into a partially evacuated five gallon glass carboy and mixed by Teflon® strips when the carboy was inverted. The resultant air mixture contained from 1 to 5 parts per million of contaminant and was drawn by the Uni-Jet Air Sampler® through a midget impinger cooled in a wide mouth Dewar flask similar to those found in most hardware stores. A second midget impinger contained the appropriate reagent to remove quantitatively any residual contaminant not held in the cold trap (Figure 1).

The same reagent and method of analysis were used: (a) to confirm the concentration of the standard solution; (b) to determine the amount of contaminant collected in the cold trap impinger; and (c) to determine the amount of contaminant not condensed in the cold trap, but carried into the scavenger midget impinger. The efficiency of the cold trap was then calculated as a percentage of the total contaminant collected. In this way sampling errors, such as non-uniform mixing of the air sample, losses from oxidation, adsorption on the sample container surfaces and sampling lines, decomposition during collection, and others, cancelled out.

Discussion

Flow through the cold trap impinger must be reversed. The vacuum source is connected to the tube of the impinger, rather than to the side arm, to prevent clogging by ice crystals which otherwise collect in the impinger orifice. Maximum freeze-out efficiency was obtained with the impinger packed to the 25 ml level with 3 mm diameter glass beads or spheres. Results satisfactory for most purposes can be obtained by installing four Teflon® baffles, of the type supplied with the Uni-Jet Lead-in-Air Analyzer,[6] equidistantly below the 25 ml graduation line on the impinger tube.

Poor collection efficiency with nitrobenzene was encountered at −21°F, the temperature of liquid Freon-12® in the Dewar flask. However, at −116°F, the temperature of liquid Freon-12® and solid carbon dioxide mixture (dry ice), effi-

Freon-12® and Teflon® are registered trade names of products of the E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware.

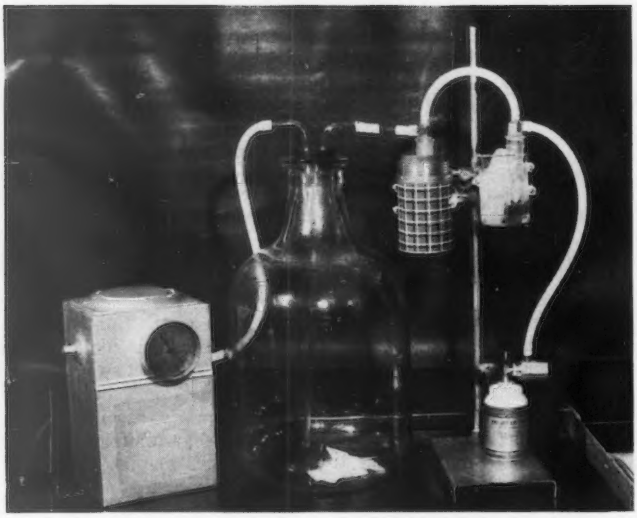

FIGURE 1. Laboratory set-up for evaluating efficiency of midget impinger cold trap.

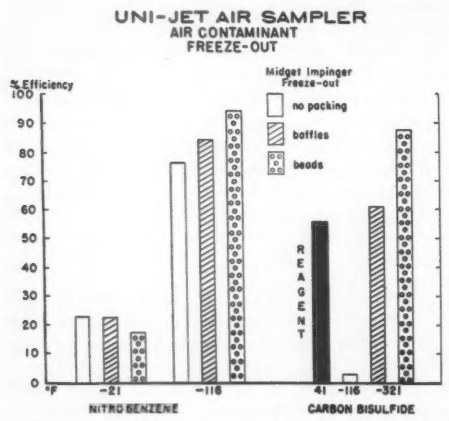

FIGURE 2. Efficiency of midget impinger cold trap sampling for nitrobenzene and carbon bisulfide.

ciencies in the 90–95% range were obtained. Liquid air temperatures (liquid nitrogen −321°F) are required to collect the more highly volatile compound, carbon bisulfide. The difference in effectiveness between glass bead packing and baffles becomes appreciable under these conditions.

Removal of water vapor by drawing the air sample through desiccants, for example, calcium chloride, calcium sulfate (Drierite), anhydrous sodium sulfate, etc., before passage through the freeze-out trap cannot be recommended for most collection problems. The contaminants sought, as well as water, are adsorbed by the dehydrating reagents. Condensation of moisture assists with the contaminant freeze-out by providing nuclei for condensation, additional active adsorption surfaces, co-precipitation (impingement) particles, and solvent action.

Data obtained from a preliminary investigation are presented in Figure 2 and Table I.

Cascade systems can be arranged for fractional condensation. A series of four traps, water-ice mixture, liquid Freon-12, liquid Freon-12 plus solid carbon dioxide, and liquid nitrogen, in order, would provide a sample separated into four fractions based on relative volatilities. The field assembly consists of a vacuum flask clamped to the Uni-Jet Air Sampler, and is small enough to be held in the hand.

Apparatus

The principle of refrigeration by evaporation and expansion of pressurized liquid Freon-12, was adapted to cool the scrubbing solution within a standard midget impinger. Liquid Freon-12 was vaporized on entering a one inch diameter coil of ¼-inch copper tubing (75 inches tube length) at the bottom, and lowered the temperature of the coil. The Freon-12 vapor passing through a Uni-Jet aspirator attached to the coil outlet created the necessary vacuum to draw the air sample through the midget im-

TABLE I

Efficiency of Collection of Vapors in a Midget Impinger Cold Trap

Using "Uni-Jet" Aspirator with 12-mil nozzle. Reversed flow through midget impinger unless otherwise noted

	Temperature °F	% Efficiency
Nitrobenzene		
Empty, normal flow	−21	37.6
Empty, normal flow	−21	14.6
Empty	−21	16.4
Empty, precooled impinger tip in liquid Freon-12	−21	32.1
Two Teflon baffles	−21	23.4
Six Teflon baffles	−21	26.0
15 ml 3-mm beads	−21	12.2
20 ml 3-mm beads	−21	14.6
20 ml 2-mm Fenske rings, normal flow	−21	30.5
Empty	−116	73.4
Empty	−116	79.2
Four Teflon baffles	−116	81.5
Four Teflon baffles	−116	85.8
10 ml 3-mm beads	−116	93.3
15 ml 3-mm beads	−116	93.2
15 ml 3-mm beads	−116	93.9
25 ml 3-mm beads	−116	94.8
25 ml 3-mm beads	−116	94.5
Effect of "Drierite" moisture trap		
Four Teflon baffles	−116	68.8
20 ml 2-mm Fenske rings, normal flow	−116	89.3
Carbon Bisulfide		
20 ml reagent, normal flow	41	55.3
25 ml 3-mm beads	−116	4.7
25 ml 3-mm beads	−116	0
Four Teflon baffles	−321	61.0
Four Teflon baffles	−321	60.5
25 ml 3-mm beads	−321	87.6

pinger. The rate air was scrubbed was dependent upon the amount of Freon-12 vaporizing in the coil, provided sufficient sensible heat was supplied to the coil.

A second coil of ⅜-inch copper tubing (85 inches tube length) was added later to provide more heating surface, and expansion capacity which was found necessary for operation at low ambient temperatures. A refrigerant drier, containing 400 mesh silica gel, also was added between the larger coil and the aspirator as an entrainment separator, and to provide additional vaporizing surface at low temperatures, Figures 3 and 4.

Several types of manually operated needle valves were found to lack the precise control required to meter a constant flow of liquid Freon-12 into the coil. A standard refrigerator valve, Detroit Controls No. 672, with a diaphragm operated by pressure on the downstream side, was found to deliver 97% of the one pound charge of Freon-12 into the coils at a constant

FIGURE 3. Photograph showing components of Uni-Jet Constant Flow Air Sampler. Parts are: (1) Uni-Jet Power Pac, (2) puncturing valve, (3) automatic control valve, (4) ¼-inch expansion coil, (5) ⅜-inch outer expansion coil, (6) additional expansion chamber, (7) aspirator, (8) midget impinger, (9) automatic control setting (covered), and (10) quick action toggle valve.

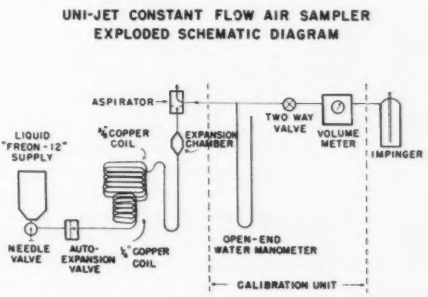

FIGURE 4.

rate. Liquid flow was adjusted by a set screw in the valve head. This adjustment has the effect of a variable aspirator nozzle orifice. Set for use with the midget impinger at 0.1 cubic feet per minute, this corresponded to an 8-mil orifice. The addition of a micrometer type valve stem control, such as Hoke micrometer kit #280-25, undoubtedly would provide reproducable rate settings.

Air volumes less than those obtained by consuming a full can of Freon-12, may be measured on a linear time basis, and controlled by a quick acting valve installed just below the aspirator.

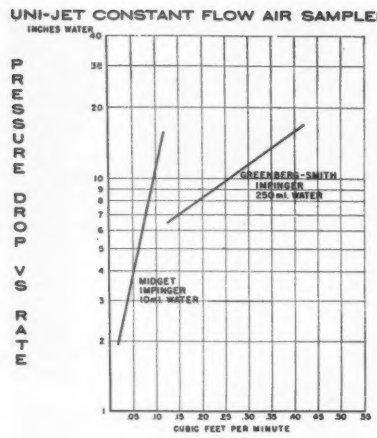
UNI-JET CONSTANT FLOW AIR SAMPLER
INCHES WATER
PRESSURE DROP VS RATE
GREENBERG-SMITH IMPINGER 250 ml WATER
MIDGET IMPINGER 10ml WATER
CUBIC FEET PER MINUTE

FIGURE 5.

TABLE II

Characteristics of "Uni-Jet" Constant Flow Air Sampler

Ambient Temp. °F	Total Volume per One Pound Freon-12	Grams Freon-12 per Cubic Foot	Total Time Minutes & Seconds	% Time at Constant Rate	Rate Cubic Feet per Minute	ΔP Inches of Water	Static Vacuum Inches of Water
Midget Impinger—10 ml water							
73	7.9	53.5	78-30	98.0	0.10	11.9	19.5
73	8.2	51.6	90-00	97.0	0.09	9.4	16.0
74	7.5	56.0	75-47	97.6	0.10	11.5	17.5
44	7.3	60.5	73-54	97.7	0.10	11.5	18.0
Greenberg-Smith Impinger—250 ml water							
74	14.4	29.1	45-25	92.5	0.33	12.4	32.0
74	14.4	31.2	44-38	98.5	0.33	12.5	31.5
74	14.6	27.5	47-17	88.0	0.35	13.3	32.0
44	part can	—	26-30	94.0	0.25	10.0	23.0

Results

Flow rate of air through the scrubber was determined by measuring the aspirator vacuum with an open end water manometer placed between the aspirator and the scrubber, and calibrated with a dry gas meter. The vacuum at this point, designated as ΔP, is related to flow in Figure 5. The static vacuum—ΔP relationship agreed within experimental error with published data.[4] The consumption of Freon-12, per cubic foot of air scrubbed, is the same as required for normal operation of the Uni-Jet Air Sampler with a 12-mil nozzle.[4]

Table II lists the characteristics of the constant rate sampler used with the Greenberg-Smith and the standard midget impingers. The "% Time at Constant Rate" variability with the Greenberg-Smith impinger may be due to operation with the expansion valve wide open for maximum flow rates, and therefore, not under control 100% of the time. The flow rate of the midget impinger was not allowed to exceed 0.1 cubic feet per minute which Roberts and McKee[3] have shown to give the maximum efficiency of the unit.

The minimum air flow through a midget impinger containing 10 ml of water, was 350 ml per minute at a ΔP of 1.7 inches. Surface tension and height of impinger liquid were the governing factors. The absolute minimum rate through an open end rotameter was 15 ml per minute. A rate of 90 ml per minute was maintained for ninety minutes through the same rotameter with a rate variation of less than ±5%. An aluminum coil required 15 to 20 minutes to reach thermal equilibrium with the surrounding air.

Summary

The Uni-Jet Air Sampler was adapted to the freeze-out technique for collecting micro concentrations of air contaminants having a wide range of volatilities. A small wide mouth vacuum flask was used to contain the coolant. The collection efficiencies for 1 to 5 ppm of nitrobenzene in air were 85% to 95% at −21°F and −116°F. Under similar conditions, the collection of carbon bisulfide required liquid nitrogen temperature, −321°F, to reach an efficiency of 85–90%.

The midget impinger was modified by reversing the flow and adding 3 mm glass beads to increase condensation surfaces. The entire sampling unit is small enough to be held in one hand, and therefore, easily portable for field work.

Volatile scrubbing solutions may be cooled below ambient temperature by vaporizing liquid Freon-12 in a coil surrounding the midget impinger, and connected to the aspirator of the Uni-Jet Air Sampler. Flow control of liquid Freon-12 into the coil by a standard refrigerator valve will produce a constant aspirator vacuum, and the effect of a variable aspirator orifice. The air flow through a standard midget impinger can be maintained at peak efficiency of 0.1 cubic feet per minute for 97% of the time required for expansion of a one-pound charge of Freon-12. The maximum constant flow through a Greenberg-Smith impinger was 0.33 cubic feet per minute while 98% of the propellant was consumed. Rates as low as 20 ml per minute at near zero flow resistance were attained.

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CERTIFICATION IN RADIATION PROTECTION

AT ITS ORGANIZATION MEETING on March 11, 1960, the American Board of Health Physics set up the procedures by which it will certify radiation protection experts throughout the United States. Under the procedures each candidate for certification will have to pass a written examination, but this examination may be waived for especially well qualified persons who apply before December 31, 1960.

A candidate for certification in Health Physics must have a Bachelor's degree in science or engineering and at least five years experience in a position of responsibility in the radiation protection field. He must be capable of making a complete radiation protection study of several types of radiation installations and will normally be asked to submit reports of typical examples of his work. He may also be required to take an oral examination in addition to the written examination.

The American Board of Health Physics was established last October by the Health Physics Society, but it will operate as an independent body. At present the Board is composed of five members, all nominated by the Health Physics Society. Other organizations will be asked to nominate additional members in the near future. The present members of the Board are Elda E. Anderson, Oak Ridge, Tennessee; J. W. Healy, Richland, Washington, J. S. Laughlin, Scarsdale, New York; W. A. McAdams, Scotia, New York and L. S. Taylor, Bethesda, Maryland. Mr. McAdams is Chairman of the Board.

The examinations, both written and oral, will be conducted by an Examination Panel which is still to be selected. Membership in the Health Physics Society is not required for certification, nor for membership on the Board or on the Examination Panel. It is expected that the first certificates of certification will be issued about July 1, 1961.

Application blanks for certification may be obtained from Dr. Elda E. Anderson, Health Physics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee. An application fee of $15 must be paid when the application is submitted to the Board and will not be returned if the applicant fails to qualify. An additional fee of $10 will be charged when certification is approved.

The Expert Witness

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THE ORIGINAL title of this paper was "The Expert Witness—Tricks of the Trade". Actually, there can be no trick in the presentation of factual evidence, and the appearance before a judicial body by an industrial hygienist is definitely not a trade but a professional activity which should embody the best efforts and the highest ethical considerations of the profession.

As a matter of fact, the term "expert witness" is somewhat of a misnomer since we are concerned as industrial hygienists with court appearances only as a confesssion of a failure to have so explained a given situation as to need judicial help in arriving at a final decision concerning the merits of any given situation.

To get back to the word "expert", I should like to point out that the connotation involves knowing a great deal about some one given matter. Therefore, in any specific situation involving a court appearance, a scientific witness should know more about the scientific and engineering details surrounding a situation than any other person. On these grounds, a scientific witness tends to disqualify himself from answering hypothetical questions which have not been based on specific examination and evaluation of the facts in the circumstances surrounding any given action.

I do not mean to say that after all the physical facts are determined, a hypothetical question could not be answered based on the observed facts in a given situation. However, when a client or an attorney writes a letter or in a conference requests that you answer certain general questions, without having examined the specific circumstances and the details thereof, and then requests a specific answer to a general hypothetical question, he is suggesting that you eliminate yourself as one expert on that specific situation. We always turn such requests down.

This matter comes up much more frequently than is generally realized. In a recent communication, the problem was stated and arrangements were suggested for arrival in court and subsequent departure all within one day's time. No time was to be allowed to make even simple tests in the area. It does not matter how much general knowledge you might have or what your scientific reputation on the topic might be, you still cannot be expert about a specific matter unless you have spent considerable time on the details surrounding specific problems.

Among the items which a scientific witness can offer to an attorney is integrity. The integrity of the scientific witness is something an attorney should not have to consider. In several cases where we have been part of a team of experts, we have heard attorneys rather plaintively ask, "but does he really believe what he is saying?"

The attorney depends almost completely on his scientific witness and if his witness is not well informed or cannot present his facts skillfully, the damage to the case is grave. We are reminded of one Ph.D. witness who had a broad range of knowledge but who presented his facts in such an involved manner that those of us who also had knowledge of the subject were completely confused even after studying the argument. This confusion may sometimes impress a jury, although we heard a juror, after one trial, remark to an attorney that "the expert sure used a lot of big words but I couldn't tell what they meant."

An unassuming and pleasant demeanor which includes the proper selection of language is the most important of all factors. The presenting of matters in a simple straight-forward manner and in very simple language is a basic requirement. We have referred to a scientific witness whose ideas were so confusing that no one could tell what he meant. Much more common is the individual who, by training, uses big words or who thinks that the use of mathematics and many-lettered words adds an aura to his cause. Nothing can be worse than to have an attentive judge say, after a long and involved scientific explanation of an air pollution problem, "Now young man, you have told us how well educated you are—will you tell us what you have been talking about?"

Simple, homely illustrations or demonstrations are wonderful if they work. We have demonstrated noise and vibration levels in courtrooms after many preliminary trial runs, and showing that the court is subjected to more annoyance than the plaintiff does not hurt your cause.

Never try anything which you are not positive will work to your advantage. In a trial

involving a fire of doubtful origin with great resulting loss, a claim against a vending company was to the effect that a short circuit in their machines had been the direct cause of the fire. From photographs and facts concerning the operation of the plant, it was much more probable that open flames under melting pots, aided by paper dust which was present in large quantity in the area where the fire presumably started, was a more likely cause. The vending machine itself indicated that it had been running and cooling long after the fire started. The attorney for the defense arranged to have a machine connected up and, without trying it out, started to demonstrate it. No sooner had he touched it than he pulled his hand back as if from electric shock. Opposing counsel then sauntered over and gingerly touched the machine and, of course, jumped back two or three feet. From that time on, there was nothing that could have been said that would have changed the verdict. The jury had seen all it needed to see.

An unbiased presentation of facts should be made. The presentation of the facts should not be exaggerated and this is not often done by scinetific witnesses. However, we were involved in one case in which a young lady was able to obtain expert psychiatric testimony to the effect that noise and vibration of less than normal traffic noise had caused her to become mentally unbalanced.

Attention to all of the pertinent details and more important, perhaps, an unflagging energy in uncovering any facts which might, in any way, bear on the problem at issue, are fundamental.

In an important action where air pollution, noise and vibration, odors and obnoxious language were all part of the complaint, a companion and I ran noise and vibration tests late one night when the wind reached an official velocity of some seventy miles an hour and the rain was heavy. During the trial a lot of fun was made by the opposition of the foolishness of running tests under such adverse conditions. Our scientific opposition agreed in court that we had been very foolish to so waste our time. However, the judge was much impressed by the readings taken in stormy weather as contrasted with readings taken under more normal circumstances. No matter how minute or seemingly unimportant a fact might seem, it should be explored in detail with the attorney.

At this point it should be made clear that the attorney is the director who has full control and whose wishes, as to what facts are to be used, are final. A scientific witness is a research assistant who does the scientific spade work and who presents those aspects of the facts which he considers useful in the conduct of his case. It should be emphasized, of course, that no reputable attorney tells you what to say. You are relied on to tell the whole truth and nothing but the truth. After an attorney, however, has decided what facts are pertinent to him, he still needs to know the entire story prior to any court appearance.

All of the above is of specific importance on the direct examination which is the presentation of the case as seen through the eyes of the attorney conducting the case. If you, as a scientific witness, have presented all the issues to the attorney, it is his primary responsibility in presenting his case to qualify you as an expert on the specific conditions under discussion. You should provide typed or printed forms listing your major qualifications to make this procedure simple and to save time.

Following the direct examination comes what is called "cross examination." Here you are completely on your own for it is at this point that it is opposing counsel's duty to attempt to prove that your case and your facts are not pertinent or sufficient. Your own attorney does not really know what you are going to say or how you are going to say it. However, if the case has been properly prepared with the proper evaluation of all of the factual data, your attorney will have a very good idea of what you will say. This will not be for the reason that he has instructed you, but because in the brutally hard process of assembling all of the facts he will have spent so many long hours with you that he will have a considerable knowledge of you as an individual.

It is during the cross-examination that the greatest test of your professional and ethical principles will arise. While it may be idealistic to do so, you should present facts in court only if you are indeed convinced beyond a reasonable doubt that the facts found represent your client's interests to the exclusion of any decision in your mind unfavorable to your cause. Your job on cross-examination is to defend yourself as an integral part of your case's defense. It is even more important to defend the facts you have revealed even at your own expense.

It is at this point in a cross-examination that a scientific witness begins to think that attorneys are mean people and, indeed, that they may have horns. I might say that personally I have the highest respect for all good trial lawyers for they not only must know their own profession, but have to become sufficiently familiar with those aspects of science and engineering which have

a bearing on the case at hand, to ask intelligent and damaging questions on cross-examination. You may have prepared lists of questions but the attorney must understand them to take advantage of any slip by the opposition.

It has been our observation that, at the end of a long drawn out tangle which may have gone on for months, the judge who has been sitting in a position of mental detachment is probably the best informed man in court regarding the facts at issue no matter how esoteric the scientific issues.

On cross-examination, it is the duty of the opposing counsel to confuse you, anger you, and in any way possible destroy the apparent value of the facts you have presented. In this sense, you are engaging in a battle of wits, and you have the right to trap the opposing counsel just as he is preparing snares for you in which to become entangled. Every situation is different and no specific advice is possible. There are several useful techniques but they all have as their purpose the persuasion of opposing counsel to the belief that you had neglected some aspect of the facts or are not well informed on some aspect of the problem. Some factual aspects of a case may either be difficult to present on direct examination or your attorney has decided to leave the matter rest until later in the case. These situations provide an unusual opportunity to present affirmative evidence in great detail at the direct request of opposing counsel. As a usual rule, the judge will protect you from being stopped, as opposing counsel sometimes attempts to do, at this stage of the proceedings.

A scientific expert's responsibility varies somewhat if he is consulted first by an attorney or by a lay client regarding a potential court action. Going to court is a last resort which attorneys try to avoid, if possible. If, as many times happens, a situation develops wherein the facts indicate a deficiency in your case, your client should be informed in all detail of these deficiencies with proper recommendations where scientific or engineering corrections are possible.

In the instance of an odor problem facing imminent community action, one of the odors from the plant was noticeable for several miles on rainy days. Investigation showed the complaint to be fully justified. We also found that this same odor, arising from pressure cooking vessels, smelled like freshly toasted cocoanut in and close to the plant, but did not smell nearly so good a mile away. When this was corrected by a special design of ventilation washer, those particular complaints ceased. Eventually, a series of engineering corrections led to such improvements that we could take the community's governing body through the rendering plant and immediately afterward take them to dinner. The plant was in such good condition that the governing body not only enjoyed the dinner, but they took no further legal action.

This method of handling nuisance cases will work for practically all such cases. Corrective procedures should be as good as can be devised economically so that once they are initiated, no further complaints should arise, or, if complaints do arise, they can be shown to be completely unjustified.

Compensation cases in which engineering and scientific studies are involved follow the same general rules in that, if the environment is shown to be safe, these facts should be presented in all the detail possible even though there has been allegation of damage to individuals. Compensation cases often involve differences of opinion among medical experts but should provoke little difference of opinion among other scientific personnel as to the actual conditions existing. If those conditions can be shown not to have existed in a different way in the past, the factual circumstances become diluted but still are useful.

In circumstances where actual injury is alleged and the surrounding facts indicate the possibility of such injury, it has been our experience that most parties concerned today are anxious that the claimant receive just compensation.

There are still differences of scientific opinion concerning the effects of various concentrations of given substances or the quantitative evaluation of injurious physical factors. If one has special knowledge of a research nature, particularly in which environmental data are correlated with medical findings on human beings, these matters should be presented with all possible vigor even though they be contrary to current opinion which may often rest upon insecure foundations.

It should be noted that there is no room for the timid soul on cross-examination. If you have your facts in hand, no amount of brow-beating or attention to side issues should sway you from your predetermined facts, and vigor in defense of these facts within the proper usage of the English language is commendable. Of preeminent importance to any profession is that the profession serves every honest interest. An expert witness who is not captive to one interest should be prepared to serve any honest case, even though that service may not always be in your own individual best interests.

There are some areas in our country where one is tagged as either a plaintiff or a defense witness. One side is not inclined to employ a person who appears for the other side. In my opinion, this violates all the rules of professional

conduct by professional people as our job is to determine facts and to present them fairly and vigorously for any honest cause.

In this connection, it should be observed that one's schedule of fees may enter into these problems, and we have had responsible plaintiff attorneys who have said that they would be glad to use our services if they could be arranged at lower rates. I do not believe that one can have two rates for two sides of a case. It is true that one has different rates for different forms of activity. At times, these rates may be too high for the amount of trouble involved. There are many ethical considerations which result from such situations.

Industrial hygienists professionally are a somewhat nonconformist group acting in the service of society. As a service group we have certain obligations. These obligations do not involve a reduction of fee where the circumstances indicate an economic deficiency, but rather a decision as to whether the merits of the situation are such that a free service or a service for out-of-pocket expense is justified whether it be plaintiff or defendant. In my opinion, this is one of the hallmarks of professional conduct. My associates and I have followed this procedure to the extent of our economic ability. We well remember spending Christmas and New Year's weeks in analyzing some fifty samples of various parts of the body of an individual whose widow was a claimant in a lead poisoning case. The body was that of a painter who had worked for a city which, for some unknown reason, refused to accept liability. A colleague and myself spent some money, as well as our time, and felt well repaid when the widow received some richly merited compensation. Before leaving the general topic, it should be clearly understood that should a situation deteriorate to the point where court action ensues, the final responsibility for determining the scientific witness fee is often in the hands of the court. We have heard of scientific witnesses receiving very nominal sums, in one case $25.00 per day, by direction of the court, for their activities.

There are times when ethical considerations dictate that you either withdraw from a case or recommend solutions which, in effect, means that you lose by default. I am particularly reminded of a large company which has been a good client and whose personnel I respect highly. In the course of determining the facts of a case in which the death of an individual was concerned and in which considerable prior investigating had been done by the corporation's own scientific staff, our findings indicated a great variance with the scientific findings of their very capable staff. This variance could have been resolved to some degree but during the course of personally ascertaining the facts, we found a situation not related to the alleged cause of the individual's death but very definitely relating to the fact that an eight story building occupied by a large number of individuals would be in danger of being blown up at almost any instant. There is always a momentary frustration when you find a situation in which extensive research and money have been spent and in which, without doubt, the defense of the claim must be completely abandoned, as the prior consideration is the immediate removal of an intolerable danger. We were able to remove the source of the danger within a day and a half, and we feel that the proper solution had, in the long run, not affected this company's regard for us.

After a string of successes, an expert witness tends to believe that all one has to do is to be honest, tell the truth in an unassuming manner, defend his convictions regarding his facts in a competent manner and that he will automatically come out on top. After a few years he finds that this is not so at all, and that on occasion when he tries his hardest and does his best, he comes out on the short end. In one or two instances, we have felt that the losses were due to a lack of trust and understanding on the part of the attorney and the scientific witness. In one instance, the attorney-in-chief had delegated the major portion of the scientific testimony examination to his second. In the few similar instances with which I have been concerned, I found the second perhaps more capable than the chief but largely restricted because of a subordinate position in the firm.

In conclusion, it should be pointed out that a good personal appearance is, of course, necessary for a professional person. It is unfortunate that sport shirts are not indicated, as many court rooms are not air conditioned. Recently, in an air conditioned court room, an engineer who was the head of a department for a major company remarked on coming down from the stand after his first half day of cross-examination, "Phew—I never knew it could be so hot up there!"

A Comparison of the Composition of Reactor Waste Solutions and Radioactive Fallout

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INDUSTRY, governmental agencies, medical and military organizations are ever increasing their use of radioactive materials. This is to be expected as a result of the expanding atomic energy program and increased availability of radioactive material from reactors and the rapidly increasing application of radioisotopes. In addition, nuclear power reactors will involve hazards not only from normal discharge of low level waste but the reprocessing of their irradiated fuel elements to reclaim the unfissioned nuclear fuel and recover the transmutation products such as plutonium-239 or uranium-233. Another source of radioactive material that has been publicized is fallout. This material results from the detonation of nuclear weapons. The scientist is concerned with the amounts and types of radioactive material produced by detonation of nuclear weapons, the mechanism involved in local and world-wide distribution of fallout, its incorporation into man's food chain, and estimation of population exposures both internal and external, including its biological and genetic effects.

Both radioactive waste and fallout have some common characteristics. The unique property of radioactivity is that there is no chemical or simple physical way to neutralize it. The contamination may be removed from the waste, or from the contaminated surface if it is due to radioactive fallout; but there is no way to prevent it from decaying. Another important fact is that radioactive compounds have chemical and physical properties which are in all respects identical to those of the stable forms of the same compounds. The radioisotopes in use are represented in all groups of the periodic table. Therefore, one can see that the universal decontaminant based on chemical properties cannot be found.

Before getting into the details of the characteristics and as a refresher some short discussion of radioactivity may be in order. As a result of nuclear fission a large amount of radioactive material is produced. This material may emit alpha or beta particles and/or gamma rays. The alpha and beta emitters are mainly only a hazard if taken internally by ingestion. The gamma emitters are primarily an external hazard. Alpha radiation is composed of positively-charged particles of the helium nucleus, which consists of two protons and two neutrons. Beta radiation consists of negatively charged particles or electrons. Gamma rays consist of an electromagnetic radiation of very short wavelength, traveling at the speed of light. Radioactivity is expressed in terms of two units. One unit is the curie which is a measure of the rate at which a radioactive substance emits particles, one curie is defined as 3.7×10^{10} disintegrations per second. This is the rate of radioactive decay of one gram of radium in equilibrium with its daughter products. The other unit is the roentgen, which is a measure of the energy dose delivered to a specific quantity of air. Roentgen is the quantity of X or gamma radiation such that the associated corpuscular emission per 0.00129 grams of air produces in air (NPT) ions carrying one electrostatic unit (esu) of quantity of electricity of either sign. However, of more practical importance is the unit called the "rad" and defined as the absorption of 100 ergs per gram of any material.

Characteristics of Reactor Waste

Irradiated reactor fuels are chemically processed to reclaim the unfissioned nuclear fuel, from mixtures of the fission products and inert components of the fuel. While processing details vary with the fuel element being processed and the plant performing the operation, the basic principles are the same (see Figure 1). This is and will continue to be the use of an aqueous solvent extraction. The aqueous raffinates from these processes will be the radioactive waste and present high-level radiation hazards for several centuries. The waste of interest now and for several years to come are: from the Purex (nitric acid), TBP-25 (aluminum-nitric acid), STR (zirconium-hydrofluoric acid-aluminum), Darex (stainless steel-aqua regia), and SIR (stainless steel-sulfuric acid) processes.[1] To standardize the types of reactor waste various researchers are working on, and to avoid the radiation haz-

Work performed at The Health Physics Division, Oak Ridge National Laboratory. Presented at the Twenty-First Annual Meeting of the American Industrial Hygiene Association, Rochester, New York, April 25-28, 1960.

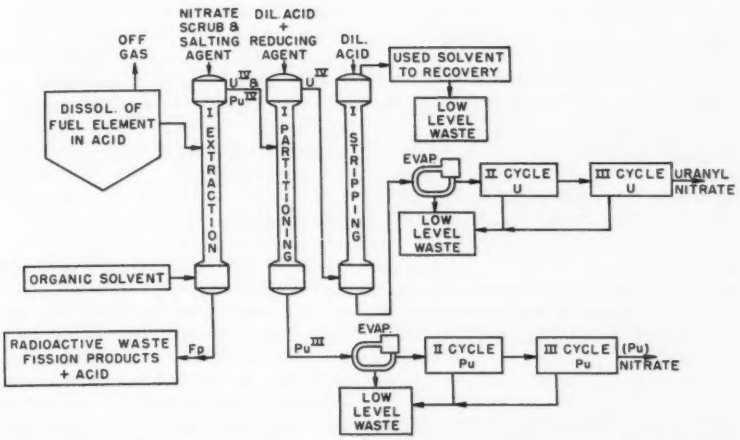

FIGURE 1. Flow chart of first cycle of a typical solvent-extraction process.

ard of the waste, it becomes necessary to prepare reliable synthetic waste. The waste solutions described below will contain more than 98% of the bulk salts present. The Purex-type waste is from aluminum-clad natural uranium fuel elements, *i.e.*, Hanford and Savannah River operations. A liter of simulated Purex waste that has been concentrated by evaporation but not neutralized, is prepared from chemicals listed in Table I, which are dissolved and then diluted to one liter.

The TBP-25 or tributyl phosphate enriched uranium waste originated from dissolving a U-Al alloy fuel element in nitric acid using a mercuric nitrate catalysis. The type of reactor using this fuel element is the Oak Ridge Research Reactor (ORR) and the Materiels Testing Reactor (MTR).

Simulated reactor waste from the TBP-25 process may be prepared from chemicals listed in Table II.

The STR or Submarine Thermal Reactor of the USS Nautilus uses a zircaloy (95% Zr + 2% Sn) clad zirconium-enriched uranium alloy core. The zirconium alloy is dissolved in hydrofluoric acid. The high level waste from this process may be simulated, using the chemicals in Table III.

One type of stainless steel waste is from the Darex process (dilute aqua regia extraction). This is used on the SM-1 (Army Package Power Reactor at Fort Belvoir) fuel elements. A liter of this type of reactor waste can be simulated using the compounds and their concentrations as shown in Table IV. The other stainless steel fuel element is the type used in the Submarine Intermediate Reactor (SIR) of the Sea Wolf. It is processed by boiling sulfuric acid then adding nitric acid to dissolve the core material. It may be simulated from the chemicals and the dosages contained in Table V. Evaporation of these acidic wastes provides the maximum reduction in volume to be secured by a simple treatment.

TABLE I

Simulated Concentrated Purex (Hanford-Type) Waste

Chemical	Amt. per Liter	Final Conc. in M
$Fe(NO_3)_3 \cdot 9H_2O$	202 g	0.5
Na_2SO_4	21.3 g	0.15
H_2SO_4	36 ml of 18*M*	0.60
HNO	353 ml of 16*M*	5.5

The radioactivity of the unneutralized concentrate after irradiation to 4000 mega-watt days per ton at a neutron flux of 5×10^{13} n/cm²/sec and cooled 100 days after discharge will be about 1300 curies/gal and emitting about 22.7 BTU/hr/gal.

TABLE II

Simulated TBP-25 Waste from U-Al Alloy Fuels (MTR., Idaho Type)

Chemical	Amt. per Liter	Final Conc. in M
$Al(NO_3)_3 \cdot 9H_2O$	600 g	1.6
$(NH_4)_2SO_4$	2.64 g	0.02
$Hg(NO_3)_2$	3.25 g	0.01
NH_4NO_3	2.4 g	0.03
HNO_3	33 ml of 16*M*	0.5

The chemicals are dissolved in water and diluted to one liter. The radioactivity of the waste is 2500 to 5000 curies/gal; the energy is 44 to 89 BTU/hr/gal (12.5–2.5) watt/gal.

TABLE III

Zirconium-Hydrofluoric Acid Waste (Nautilus Type)

Chemical	Amt. per Liter	Final Conc. in M
$Zr(OH)_4 \cdot 12H_2O$	206 g	0.55
$Al(NO_3)_3 \cdot 9H_2O$	273 g	0.75
$Cr(NO_3)_3 \cdot 9H_2O$	6.4 g	0.016
Sn	1.43 g	0.012
HF	107 ml of 28*M*	3.0
HNO_3	83 ml of 16*M*	1.3

The radioactivity of the waste from a reactor of this type subjected to the irradiation, flux, cooling time, etc., mentioned for the Purex waste, would be 100 curies/gal; the energy would be 1.71 BTU/hr/gal (0.5 watts/gal).

TABLE IV

Darex-Stainless Steel Plus Aqua Regia (Army Package Power Type) Waste

Chemical	Amt. per Liter	Final Conc. in M
$Ni(NO_3)_2 \cdot 6H_2O$	19.8 g	0.075
$Fe(NO_3)_3 \cdot 9H_2)$	275 g	0.68
$Cr(NO_3)_3 \cdot 9H_2O$	64.0 g	0.16
$Al(NO_3)_3 \cdot 9H_2O$	46.1 g	0.123
HCl	1 ml of 1*M*	0.001
HNO_3	189 ml of 16*M*	2.95

The activity of this waste subject to the conditions assumed for the other fuel elements would be about 1000 curies/gal and the energy about 17.5 BTU/hr/gal.

TABLE V

Stainless Steel-Sulfuric Acid Waste, SIR (Sea Wolf) Type

Chemical	Amt. per Liter	Final Conc. in M
$Fe(NO_3)_3 \cdot 9H_2O$	28 g	0.07
$Ni(NO_3)_2 \cdot 6H_2O$	2.3 g	0.008
$Cr(NO_3)_3 \cdot 9H_2O$	13 g	0.018
$Mg(NO_3)_2 \cdot 6H_2O$	4.4 g	0.017
H_2SO_4	28 ml of 18*M*	0.51
HNO_3	131 ml of 16*M*	2.35

The activity of this type of a first cycle raffinate would be about 1500 curies/gal. or 7.5 watts/gal.

Neutralization using caustic-produced solid precipitates of ferric, aluminum, or zirconium hydroxide which settle slowly and are difficult to filter.

A characteristic distinguishing radioactive wastes in general from any other industrial wastes, and which makes them perhaps more dangerous on being released to the air, soil or waterways, is that the harmful associated radiations are not detected by the human senses. However, appropriate instrumentation and radiometric analysis will reveal the nature and character of these contaminants with great accuracy. The toxicity of radioactive wastes to humans is much greater proportionally than that of other types of industrial poisons. High-level radioactive waste solutions are different from the much publicized radioactive fallout, physically and chemically.

Characteristics of Fallout

Fallout has been the subject of many investigations both scientific and political for several years. Contaminated particulates in a cloud of radioactive material is transferred to ground surfaces, buildings and vegetation by fallout, washout, and rainout. It is customary to use fallout as the collective term and also to designate the particulate radioactive matter deposited.

In general, it is agreed that the ionizing radiation associated with this material is hazardous both somatically and genetically. The great controversy arises from the degree of hazard and the quantitative long-range genetic effects. Fallout consists of: (a) the fission products; (b) weapon vehicle such as bomb case, missile, shot tower, etc.; (c) neutron-induced activated elements; (d) geologic material from the vicinity of ground zero or the crater. However, the neutron-activated material contributes only a fraction of a per cent of the total or gross residual radioactivity compared to the fission products.[2]

In the case of the detonation of a nuclear device, the term residual nuclear radiation is applied to the radiation emitted by fission products, neutron-activated material, and uranium or plutonium which has failed to fission. In the case of an incident involving a critical assembly, *e.g.*, a reactor excursion, the radioactive fallout has physical characteristics similar to those produced by a nuclear weapon. When an accident to a power reactor is the cause of the release of fission products, the physical characteristics are different because of the relative low amount of neutron-induced radionuclides, and because of the controlled fission within the reactor, which results in a relative low ratio of short lived fission fragments and a relative abundance of long lived fission products.

Therefore, the decay rate of the mixture or rate at which radiations are emitted by the radioactive material is dependent upon the source of its production. Due to the slower decay rate of the mixture, the fission products released by an accident to an operating reactor, or from high level radioactive waste, are more dangerous than the same quantity (number of curies) released from a weapon.

Neutrons resulting from the detonation of a nuclear device induce radioactivity in various normal nonradioactive materials. Most of the induced radioactive material is short-lived and contributes to the rapid decay rate of fallout.

Fallout from nuclear weapons detonated over land masses is comprised of particles whose radioactive components are made up in the form of melted silica spheres. These radioactive silica spheres have an extremely low solubility in water and most mineral acids. Therefore, the radioactive fission products associated with them will not be released into the aqueous media. Due to fractionation within the nuclear cloud, smaller particles which are deposited further downwind will have some of the more volatile fission products in vapor state longer, condensing on their surfaces. Experimental data indicate that these radioelements are more water soluble and will be released into both water and acidic solutions. The long-range fallout and particles formed from a water-soluble matrix are entirely different substances. Therefore, where the radioactive material is adsorbed or condensed on the surface, it can be leached or dissolved by an aqueous medium.

The radioactive particles in the stratosphere have to move into the lower layer, the troposphere, before they can be brought down by precipitation.

In addition to the precipitation process fallout is also brought down as dry dust through turbulent deposition. This is not due to gravitation, but to eddy currents and Brownian movements which bring the particles in contact with surfaces on which they stick. The rate of this deposition becomes proportional to the free surface area, the air concentration and the average velocity of the particles. In ordinary gaseous diffusion this velocity is given by the temperature and the mass of the particle. The rate of deposition in a collector also depends upon the turbulence of the air, which, among others is very dependent upon the shape and surroundings of the collecting device. Stewart *et al.*[3] have determined an effective velocity—the velocity which multiplied by air concentration gives the rate of deposition—over horizontal sheets of gummed paper. They find that this rate of deposition is small compared to the cumulation caused by atmospheric precipitation.

It has been determined that nuclear weapons can contaminate the soil, the magnitude and extent of the contamination varying widely with the size and type of weapon and methods of employment. For estimating the degree of solubility of fallout in water, it appears conservative to assume that ten per cent of the contaminant in the soil will be water soluble.[4] Since the fraction in solution in a given sample is not directly related to the amount in suspension, it is not possible to measure the total fallout contamination in a turbid water sample and estimate the fraction in solution.

However, a more important aspect with respect to the problem of decontamination is the interactions that take place between silica particles and surfaces. For regions of significant levels of fallout, the particle size of importance is 75 μ and larger as these carry the larger fraction of the radioactive contaminant. Therefore, any decontamination process that removes these particles from the surface of the material to be decontaminated also removes the radionuclides which are fused within the particles.

As fallout consists mainly of nonradioactive debris from nuclear detonations, the essential physical and chemical behavior of fallout is determined by the nature of the inert debris. For example, fallout from detonations on surface of the ocean will consist of sea water, construction materials of the weapon, and radioactive materials; while fallout from a land-surface burst is produced from soil and target materials, weapon-construction materials, and radioactive elements. In terms of mass, or weight, the relative abundance of the radioactive elements is much less than one part in a billion. Therefore, except for their radioactive properties, these elements would be extremely difficult to detect.

Accordingly, all major physical and chemical processes which deal with fallout require knowledge on the relation of radioactive material with the bulk material. The simplest of these relationships is the ratio of radioactive material to the gross mass or its inverse.[5]

Mackin *et al.*[6] stated that coral particles could be grouped into two broad categories, altered and unaltered, depending upon whether the physical appearance of the coral particle resembled a spherical or flaky (altered) shape or an angular or irregular (unaltered) shape. However, it should be realized that such divisions are not sharply bounded since differences exist between particles in a single class. Although the number and size ranges of the two categories of particles may vary with time and point of fallout, particles of the same category have similar radioactive composition.

The actual elements produced as fission products are all the elements from gallium to hafnium (atomic numbers 31 to 72) in the periodic chart. It is estimated that a 20 KT explosion produces some 6000 million curies of activity at H+1 hr. This includes about 200 isotopes of over 35 elements with half-lives of fractions of

a second to decades. Based on the relative hazard expressed in terms of the maximum permissible concentration, strontium-90 is the most important long-term contaminant. The total dissolution of the Sr^{90} produced from a 20 KT burst in water would require two million acre feet (43,560 cu ft = 1 acre ft) to dilute the activity to drinking water tolerance.

The biological importance of the dissolved contaminant must be evaluated in terms of the characteristics of the radionuclides present, length of exposure time (*i.e.*, water ingestion period), and acceptable limits of human tolerances. It is to be emphasized that tolerances used in an emergency must take into consideration the factor of human necessity, and these tolerances will be higher than what is considered acceptable in peacetime. Based on the available limited data, it does not appear that the dissolved radioactive fallout to be encountered under wartime conditions will greatly exceed the present emergency tolerance levels. No rational explanation is available for the wide range of indicated solubilities, obtained in various studies, except there is a wide variation in weapon types, weapon design, soil types, shot conditions, meteorological conditions, etc., and very small amounts of radioactive materials compared to the inert debris, about 2 lbs of fission products from a Hiroshima-type weapon.

The more soluble elements, unless incorporated into an insoluble carrier, are most likely to be transported in the environment and to pass most conventional water treatment processes. Strontium, iodine, and cesium are in the soluble group. The radio-elements that exhibit a tendency to form hydrous oxides are incorporated in the particulate or colloidal fraction. In addition, these nuclides would occur in natural waters as particulates and would be removed by conventional water treatment procedures, while radiostrontium and radiocesium in general exist in the ionic form and are more difficult to remove by coagulation. The decay parameter for a fallout fission product mixture varies from 1.25 to 1.03 between one and 100 days after detonation[7] due to environmental fractionation and is generally taken as 1.2.

From the viewpoint of internal damage by ingested material contaminated with fallout, the important or hazardous fallout fission products are: iodine-131, barium-140, strontium-89 and -91, which are also high-yield fission products.

Tolerances for both external and internal long-term hazards have been established for peacetime exposures and can be found in the National Bureau of Standards publications.[8, 9]

The present theories of atmospheric circulation only give an approximate picture of the situation, a number of details are lacking, *i.e.*, degree of mixing and separation of the fallout components, from the time the explosion takes place, till the time when the sample is collected. There are indications that the mixing is incomplete and that chemical separations do take place. As long as the magnitude of these effects is not known, little confidence can be placed in information given about single isotopes calculated from total activities. It further applies to the rates of transfer from the stratosphere to the troposphere and from the troposphere to the ground.

Summary

As is evident from the above discussion both fallout and power reactor wastes constitute hazards to the population. All radiation is damaging, however, the relative danger will depend on the length of time and level of exposure. Hazards due to radiation and chemical toxicity in a chemical processing plant under conditions of normal operation can be controlled. General radiation levels for radioactive fuel processing equipment can be reduced with proper shields. Ingestion and inhalation of radioactive material either reactor-produced or from the fallout of a nuclear detonation may be detected and controlled.

The major biological hazards in the reactor waste after a 30-year accumulation period and a 5-year decay following accumulation, are the fission products in the following order: Sr^{90}, Cs^{137}, Ce^{144}, Pr^{144}, and Pm^{147}. All these radionuclides are also formed in a nuclear detonation and are the most hazardous of the long half-life fission products in fallout, as well as in reactor waste. Chemically, both qualitatively and quantitatively, the accompanying or carrier material usually is a different compound.

This is the type of complicated, diversed problem involving many fields of science that members of the American Industrial Hygiene Association have been dealing with and will continue to be challenged with for some time to come.

Acknowledgment

The author wishes to thank H. N. Lowe, Jr., and D. C. Lindsten of the Engineer Research and Development Labs., Fort Belvoir, Va.; F. M. Empson and I. R. Higgins of the Oak Ridge National Lab.: and personnel of the Chemical Technology and Health Physics Divisions, ORNL; and the Physical Sciences Division of OCDM, for their cooperation, advice, and technical aid.

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Eighth Detroit Anachem Conference

THE EIGHTH DETROIT ANACHEM CONFERENCE will be held at McGregor Memorial Conference Center at Wayne State University on October 24–26, 1960. The full program has been released showing an offering of a fine variety of 65 papers, many of which are of significance to the industrial hygiene chemist. All papers of the sessions on General Analytical Chemistry, and Clinical and General Analytical Chemistry will be of interest and most will be of direct use. The discussions of analyses by neutron activation are intriguing for their novelty and promise of a useful new technique. Likewise many applicable ideas are to be presented at the sessions on flame photometry, absorption and emission spectroscopy, gas chromatography, x-ray fluorescence, solvent extraction, and polarography. A feature of the program will be the presentation of the Anachem Award for Outstanding Achievement in Analytical Chemistry to Harry A. Bright.

For information and advance registration write to Dr. D. A. Keyworth, Research Department, Wyandotte Chemicals Corporation, Wyandotte, Michigan.

Industrial Health Nursing

A FULL-TIME, ONE-WEEK COURSE for nurses in industrial health will be given beginning October 31, 1960, by the Department of Industrial Medicine of New York University Post-Graduate Medical School, of the New York University Medical Center. The course, limited to 50 nurses engaged in industrial nursing, will be given under the direction of Dr. David H. Goldstein, professor of industrial medicine at the Post-Graduate Medical School.

Instruction consists of lectures and conferences led by both medical and nursing faculty of the Medical Center. A field trip of half a day will permit a visit to and a study of an industrial medical department in the Greater New York area. Subjects to be covered during the week include: occupational health nursing as viewed by management, the physician and the nurse; the small plant problem; communications and supervision; individual and group behavior in an industrial setting; counselling and interviewing techniques; labor relations; preparation for retirement; and problem clinic. Several sessions will be held jointly with industrial physicians enrolled in postgraduate study.

Applications should be sent to the Dean, New York University Post-Graduate Medical School, 550 First Avenue, New York 16, New York. Mention course 484. The tuition is sixty dollars.

Air Flow Calibration of Direct Reading Colorimetric Gas Detecting Devices

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RECENT years have seen the widespread introduction of devices for making rapid, simple, and more-or-less accurate estimates of the concentration of air-borne gas and vapor contaminants. Certain devices, of which the carbon monoxide detector is probably the best-known, make use of the color change which occurs upon the reaction of the gas in question with the specific chemical reagent. The Occupational Health Field Headquarters of the Public Health Service has undertaken a testing program of the instruments currently available. This article describes some of the early results of that program.

At present (March, 1960) there are four major suppliers of kits for testing for a variety of gases. Three of the four kits which are now available use a single air moving device and separate detecting tubes for each gas. One company manufactures a kit in which the air moving device and color indicator are sold as a unit.

The air moving devices used with these detector kits are important factors in the over-all performance in gas and vapor analysis. Experience in this laboratory indicated that the reliability of the pump might be open to question. A report from South Africa[1] also questioned pump reliability.

Pump A is a bellows device which has a nominal capacity of 100 milliliters. The rate of flow through the sampling tube is a function primarily of the packing of the tube in that the only resistance to the flow is offered by the tube itself. When the bellows are squeezed, air is expelled through a rubber diaphragm valve. On the intake cycle the valve completely covers the exit port thereby permitting entry of air only through the inlet. It was found that pumps which had been in use for as little as six months, and in one instance a new pump, the diaphragm did not operate properly. This was due to either (a) the diaphragm being off-center and thereby not completely covering the exit port, or (b) aging of the rubber used in the diaphragm and subsequent loss of flexibility. However, replacement of the exit diaphragm valve is rather simple and in every case it was possible to restore the nominal air flow through the sampling tube. Of eight properly operating, new or repaired, pumps tested, the average volume was 101.8 milliliters. The capacities ranged from 98.5 to 103.8 milliliters. This is considered to be well within reasonable limits of accuracy for such a sampling device.

Pump B consists of a cylinder to which has been fitted a hand-honed piston. Nominal capacity is 100 milliliters. In its present modification a critical flow orifice is placed between the sampling tube and the pump to insure constant flow for the greater part of the sampling period. The pump has undergone several transitions since it was introduced into this country and the tests for pump reliability have reflected these. In early models it was found that there was leakage in the exit valve; air flow through sampling tubes was as low as 60 per cent of nominal capacity. Four models of the presently distributed variety each showed air flows varying approximately 2 per cent from the nominal value which is well within the 5 per cent tolerance limit claimed by the manufacturer. Operating instructions for the detection of toxic gases specify a given time period in which air flow must be maintained. Variations in orifice size would lead to errors due to altered air flow characteristics. Examination of the orifices on Pump B showed that they were not properly machined. The manufacturer subsequently informed this laboratory that closer quality control would be maintained.

Pump C is operated by a squeeze bulb of 50 ml capacity. Air flow is regulated by an orifice which can be varied. According to the manufacturer's instructions the bulb should refill within 30 seconds ± 3 seconds. It is a simple matter to adjust the orifice so that the bulb fills in the designated time. The South Africans found, however, that "... aspiration ceased approximately 15 seconds after the bulb had apparently expanded to its original volume."[1] Our

Based on work supported by the Bureau of Ships, Department of the Navy, under Contract No. S23 (649B) Ser. 649B-333 dated February 25, 1959.

tests confirmed these findings. Air continued to be drawn into the bulb for varying lengths of time up to 20 seconds. The additional volume was found to reach as much as 15 ml or 30 per cent of the nominal capacity of the bulb.

Pump D, in the newest of the kits, is also a squeeze bulb of 50 ml nominal capacity. The bulb appears to be completely inflated in 15 to 20 seconds. Actually, flow continues for an additional 10 seconds. The additional volume drawn in that time was found to reach as much as 9.5 ml or 19 per cent of the nominal capacity of the bulb.

The possibility of variation in flow rates through the several sampling devices and that of deterioration of flow control mechanisms, with resultant change in flow patterns, makes it necessary that a means for calibrating air flow be provided, especially for field use. A rather simple instrument has been devised for this purpose. A buret with a capacity of approximately 125 milliliters was constructed from ¾-inch I.D. thin-wall (1/16 inch) plastic tubing. The capacity of the buret between 90 and 100 milliliters was marked off in one ml divisions by using a volumetric pipette and filling the buret with successive known quantities of water. A nipple was sealed to the top of the plastic tube to facilitate the attachment of rubber tubing; the entire assembly was then ready for calibration of the pumps. Figure 1 shows the calibration assembly.

A solution of synthetic detergent and water was made, and the resultant foam permitted to subside. The solution was then poured into the buret very carefully to avoid raising additional foam and then reemptied in such a manner that the inside walls of the buret were coated with a thin film of the soapy water. The open end of the buret was then placed momentarily in contact with the surface of the soapy water; when withdrawn a soap film adhered to the mouth of the buret. Upon the application of suction the soap bubble could be pulled up through the length of the buret.

The friction between the wall of the buret and the soap bubble is negligible. It was found, for example, that pressures of 0.02 inch of water were all that were needed to move the soap bubble. This "frictionless piston" is portable, readily constructed and unbreakable. All that is necessary in the calibration procedure is to start the soap bubble at the reference point, draw air through a sampling tube by means of the particular aspirating device under test and note the total volume after the bubble has come to equilibrium.

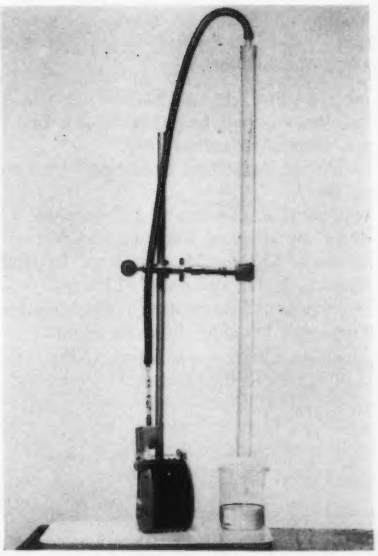

FIGURE 1. Field calibration assembly showing the plastic bubble meter attached to one type of sampler.

Summary

The necessity for checking carefully the air flow characteristics of direct reading colorimetric gas detecting devices has been shown. Construction of a simple buret using a soap bubble as the indicating medium has been described. Such a device could be made part of field equipment.

Acknowledgment

The author gratefully acknowledges the assistance of Robert Helmling in the construction of the buret and in the calibration of several of the pumps. Mr. Marshall LaNier photographed the equipment.

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News of Local Sections

New England Section

The May meeting of this Section was an all day session devoted to papers and a panel discussion. Papers presented were:

"Industrial Parathion Poisoning" by Leonard Pagnotto

"Acoustical Enclosures of a Pneumatic Tamping Press" by Richard Johnson, and Stanley Pihl

"A Case of Chronic Mercurialism" by Heinrich G. Brugsch, M.D., and John P. Fahy

"Two Cases of Manganism in the Manufacture of Manganese Dioxide" by John Skinner

"Phenol in Urine as an Index of Benzene Exposure" by Janet Walkley, and Leonard Pagnotto

A panel discussion of "Industrial Hygiene Aspects of a Nuclear Facility" was presented by E. T. Borowski, G. S. Golden, R. L. Hancock, R. L. Hoover, and R. L. Layfield.

Michigan (Detroit) Section

At the Annual AIHA Banquet in Rochester, President Paul Giever presented the Annual Michigan Section Award for the best paper appearing in the AIHA Journal during the preceding calendar year.

Officers and Executive Committee members for the coming year are: Paul M. Giever, President; Donald L. Eschelbach, President-Elect; Vincent J. Castrop, Past-President; Jerome K. Brasch, Secretary-Treasurer; Robert S. Ajemian, Edwin F. Braun, William F. Cleary, John H. Ganschow, M.D., James W. Lake, James D. MacEwen, Marion A. Mills, R.N., and John V. Roest, members of Executive Committee.

At the March meeting Dr. H. E. Stokinger, Occupational Health Program, U. S. Public Health Service, spoke on the subject of "Toxicological Interaction of Air Contaminants."

The May meeting consisted of an all day conference sponsored jointly with the Western Michigan and Northeast Michigan Sections of AIHA.

Western Michigan Section

The May meeting was a joint industrial health conference sponsored in cooperation with the Michigan (Detroit) Section and the Northeast Michigan Section. The meeting was attended by 95 people and the program included the following papers:

"Respiratory Protection" by S. J. Pearce

"Chemical and Biological Warfare" by Col. George C. Rich

"A New Classification of the Pneumonconioses: Their Development and Clinical Significance" by Seward E. Miller, M.D.

"Practical Solutions to Industrial Noise problems" by James H. Botsford

"Experiences in the Design and Use of Enviree —An Instrument for Measuring Environmental Physical Factors" by Andrew D. Horsey.

Northern California Section

At its annual meeting the Section elected officers for the 1960–61 year. Benjamin Linsky was elected as President-Elect, Guido Rosati as Secretary-Treasurer, and Albert L. Baietti as a new member of the Board of Directors. Dr. James Hughes ascends to the position of President succeeding Robert Owens. Robert Mendell was appointed publicity chairman for the Section.

The speaker for this meeting was Dr. James A. Spence, Industrial Hygienist, Standard Oil Company of California. He spoke about the development of Standard Oil Company's industrial hygience program.

Philadelphia Section

The May meeting of this Section was a field trip to Paulsboro Laboratories of the Socony Mobile Oil Corporation. The program included a tour of the laboratories, a talk on the operations, and an excellent smorgasbord dinner. At the business meeting officers for the coming year were installed.

Obituary

Manfred Bowditch, director of health and safety for the Lead Industries Association since 1948, died at his New York home on June 29, 1960. He was formerly field director of the Saranac Laboratory and for many years was director of the Massachusetts Division of Occupational Hygiene. A graduate of Harvard University, he had also held teaching posts at Harvard and at Tufts. He was a charter member and director of AIHA, also a member of APHA, ACGIH, APCA and other professional societies. We all take regret in the death of this always stalwart and often fiery proponent of industrial hygiene.